Near Infra-Red emission from a *mer*-Ru(II) complex: consequences of strong σ-donation from a neutral, flexible ligand with dual binding modes

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Electronic Supporting Information

- ## Materials, methods and instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded in CD_3CN at room temperature (r.t.) on a Bruker AV400 (400 MHz) and AV700 (700 MHz) spectrometers (as noted in the experimental) for ^1H NMR and at 100 and 175 MHz (as noted in the experimental) for ^{13}C NMR, respectively. 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** was 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 ($\Phi = 0.23$)[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). Electrochemical measurements were carried out in argon-purged purified acetonitrile at room temperature with a BAS CV50W multipurpose equipment. 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 of **L1**, **1** and **2** were obtained at scan rates of 100, 50 and 25 mV s^{-1}, respectively. 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. Differential pulse voltammetry was conducted with a sweep rate of 20 mV s^{-1} and a pulse amplitude, width and period of 50 mV, 50 ms and 200 ms, respectively.

Experimental uncertainties are as follows: absorption maxima, ±2 nm; molar absorption coefficient, 10%; redox potentials, ± 10 mV; emission maxima, ±4 nm; emission lifetimes, 10%; emission quantum yield, 20%.

1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-α]pyrimidine (**H-hpp**), 2,6-dibromopyridine, (±) BINAP, *t*-BuOK were purchased from Aldrich and used as received. Cyanine IR-125 was purchased from Acros Organics. Ph-tpy[3] (Ph-tpy = 4′-phenyl-2,2′:6′,2′′-terpyridine), $Ru(DMSO)_4Cl_2$,[4] $RuCl_3$(*i*PrSPh)$_2$(CH_3OH)[5] were synthesized using literature procedures.

• Synthetic Details

Synthesis of **L1**:

(±) BINAP (0.06 mmol, 38 mg) was placed in an oven dried round bottomed flask purged with nitrogen which was sealed with a septum. Dry toluene (3 mL) was added via syringe. The resulting suspension was heated at 90 °C for 2 min to dissolve the BINAP. This was cooled to room temperature and $Pd(OAc)_2$ (0.04 mmol, 9 mg) was added and stirred for 3 min. To the resulting bright yellow solution, 2,6-dibromopyridine (2 mmol, 474 mg) and 1,3,4,6,7,8-

hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (4.3 mmol, 600 mg) were added. Stirring for 5 min at ambient temperature resulted in a pale orange slurry to which was added *t*-BuOK (5.6 mmol, 640 mg). The reaction mixture was then stirred at 90 ^{o}C for 3.5 h, was cooled to room temperature and diethyl ether (60 mL) was added and the mixture was filtered. Evaporation of the filtrate afforded the ligand (**L1**) as crystalline pale yellow solid. Single crystals suitable for X-ray crystallography were grown by slow evaporation of a diethyl ether solution of the compound. Yield = 563 mg (80 %). ^{1}H NMR ($CDCl_3$, 400 MHz); 7.34 (t, J^{t} = 8 Hz, 2 H), 7.11 (d, J^{d} = 8 Hz, 2 H), 3.83 (t, J^{t} = 6 Hz, 4 H), 3.40 (t, J^{t} = 6 Hz, 4 H), 3.21 (t, J^{t} = 6 Hz, 4 H), 3.14 (t, J^{t} = 6 Hz, 4 H), 1.95 (quint., J^{qt} = 6 Hz, 4 H), 1.86 (quint., J^{qt} = 6 Hz, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz); 154.5, 150.2, 136.6, 110.4, 48.8, 48.6, 43.9, 43.6, 23.7, 22.8 ppm. HRMS (ESI), m/z: 117.62399 $[M+2H^{+}]^{2+}$ ($C_{19}H_{29}N_7$ requires 177.62367), 354.24006 $[M+H^{+}]^{+}$ ($C_{19}H_{28}N_7$ requires 354.24007), 376.22216 $[M+Na^{+}]^{+}$ ($C_{19}H_{27}N_7Na$ requires 376.22201). Anal. Calc. for $C_{19}H_{27}N_7$ + 1 H_2O : C, 61.43; H, 7.87; N, 26.39. Found: C, 61.57; H, 7.95; N, 26.53.

Ru(Ph-tpy)Cl₃

Ph-tpy (100 mg, 0.323 mmol) and $RuCl_3$(*i*PrSPh)$_2$(CH_3OH) (185 mg, 0.339 mmol) were refluxed in air for 18 h in CH_3CN (60 mL). After cooling down to r.t., the solvent was evaporated to dryness under vacuum. The dark purple solid obtained was sonicated with EtOH (10 mL) and EtOAc (50 mL) and filtered. The solid product was then washed with EtOH (10 m L) and Et_2O (2 x 30 mL) and dried under vacuum to give the product as brown solid (160 mg, 96%) and used without any further purification. ^{1}H NMR (DMSO-*d₆*, 400 MHz); 9.69 (s, 2 H), 7.34 (s, 2 H), 0.77 (s, 1 H), -1.07 (s, 2 H), -2.52 (s, 2 H), -9.21 (d, J^{d} = 80 Hz, 4 H), -35.53 (br, s, 2 H) ppm.

*[Ru(Ph-tpy)(**L1**)](PF$_6$)$_2$* (**1**)

A mixture of [Ru(Ph-tpy)Cl$_3$] (100 mg, 0.193 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, to the suspension was added **L1** (72 mg, 0.203 mmol) and the resulting mixture was refluxed for 12 h under nitrogen atmosphere. After 12 h, the dark purple mixture was cooled down to ambient temperature and solvent 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 cryatallography were grown by diffusion of diethyl ether into a moderately concentrated solution of the complex in acetone. Yield = 75 mg (37%). ^{1}H NMR (CD$_3$CN, 700 MHz); 8.69 (s, 2 H) 8.54 (d, J^d = 8.0 Hz, 2 H), 8.14 (t, J^t = 8.0 Hz, 1 H), 8.09 (dd, J^d = 8.0 Hz, J^d = 1.0 Hz, 2 H), 8.05 (dd, J^d = 6.0 Hz, J^d = 1.0 Hz, 2 H), 7.99 (td, J^t = 8.0 Hz, J^d = 2.0 Hz, 2 H), 7.67 (t, J^t = 7.0 Hz, 2 H), 7.58 (t, J^t = 7.0 Hz, 1 H), 7.48 (m, 4 H), 4.04 (m, 2 H), 3.58 (m, 4 H), 3.20 (m, 2 H), 3.05 (m, 4 H), 2.32 (m, 2 H), 2.11 (m, 2 H), 1.67 (m, 2 H), 1.45 (m, 2 H), 1.21 (m, 2 H), 0.85 (m, 2 H) ppm. ^{13}C NMR (CD$_3$CN, 175 MHz); 159.8, 158.8, 155.9, 154.0, 153.9, 143.7, 140.8, 138.2, 137.1, 130.5, 130.3, 128.2, 126.9, 123.9, 120.9, 112.8, 49.6, 48.8, 48.4, 43.8, 23.3, 23.1 ppm. HRMS (ESI), m/z: 909.22556 [M-PF$_6$]$^+$ ($C_{40}H_{42}N_{10}PF_6Ru$ requires 909.22737), 382.13215 [M-2PF$_6$]$^{2+}$ ($C_{40}H_{42}N_{10}Ru$ requires 382.13132). Anal. Calc for $C_{40}H_{42}N_{10}RuP_2F_{12}$: C, 45.59; H, 4.02; N, 13.29. Found: C, 45.68; H, 4.08; N, 13.03.

*[Ru(**L1**)$_2$][(PF$_6$)$_3$]* (**2**):

A mixture of Ru(DMSO)$_4$Cl$_2$ (50 mg, 0.103 mmol) and **L1** (75 mg, 0.211 mmol) in nitrogen-degassed ethylene glycol (15 mL) was heated at 200 °C for 2x10 minutes in microwave to give a dark brown solution. After cooling down to ambient temperature, solvent was evaporated to dryness. The chloride salt was metathesized to the PF$_6$ salt by addition of excess of saturated aqueous KPF$_6$ solution to the aquous solution of the compound. The resulting brown solid was collected by filtration, washed with water (3x20 mL) and dried under vacuum. The product was purified by silica column chromatography using acetonitrile:saturated aq. KNO$_3$ (5:2, v/v) as eluent. Crystals suitable for X-ray cryatallography were grown by diffusion of diethyl ether into a concentrated solution of **2** in acetone. Yield = 90 mg (80%). ^{1}H NMR (CD$_3$CN, 400 MHz); 27.65 (br, s, 2 H), 18.25 (br, s, 2 H), 8.39 (br, d, J^d = 169.6 Hz, 8 H), 7.09 (br, s, 4 H), 4.59 (br, s, 6 H), 2.99 (br, s, 8 H), 1.46 (br, s, 12 H), 0.54 (br, s, 4 H) 0.09 (br, s, 4 H), -1.02 (br, s, 4 H). ^{13}C NMR (CD$_3$CN, 100 MHz); No peaks were observed due to paramagnecity of the complex. HRMS (ESI), m/z: 1098.29753 [M-PF$_6$]$^+$ ($C_{38}H_{54}N_{14}RuP_2F_{12}$ requires 1098.29775), 476.66801 [M-2PF$_6$]$^{2+}$ ($C_{38}H_{54}N_{14}RuPF_6$ requires 476.66651), 269.45732 [M-3PF$_6$]$^{3+}$ ($C_{38}H_{54}N_{14}Ru$ requires 269.45610). Anal. Calc for $C_{38}H_{54}N_{14}Ru_1P_3F_{18} \cdot 3C_3H_6O$: C, 39.83; H, 5.12; N, 13.84. Found: C, 39.61; H, 4.80; N, 13.51.

Although after column chromatography and recrystallisation of complex **2**, the thin-layer chromatography dispalyed a single spot, formation of trace amount of homoleptic *mer*-isomer may not be excluded.

- **NMR Characterisations**

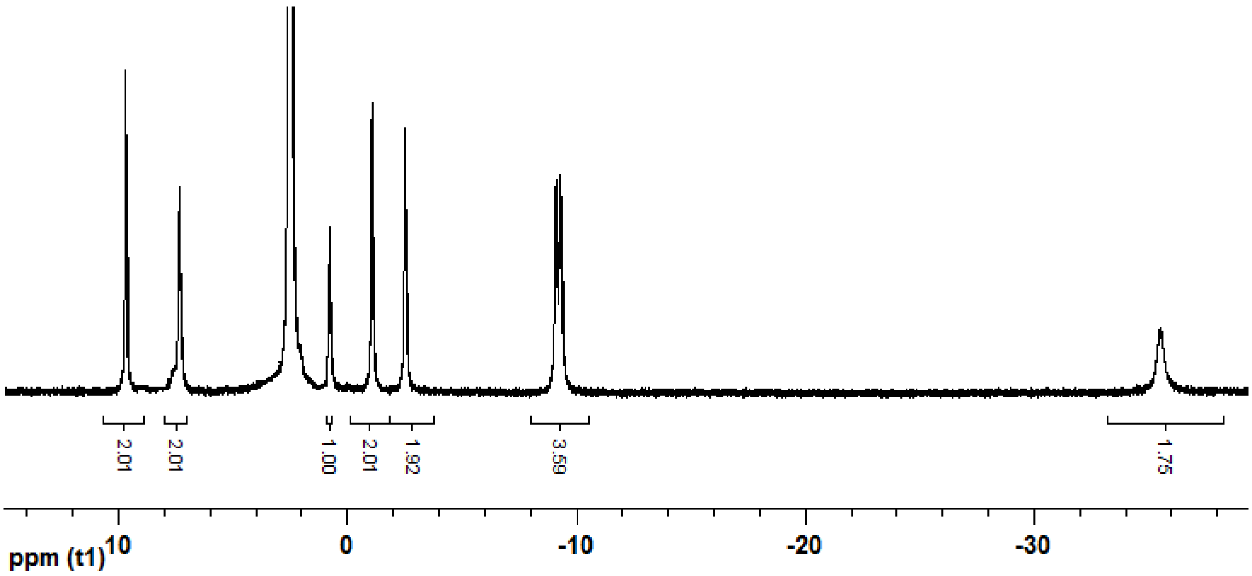


Figure S1. ^{1}H NMR of *Ru(Ph-tpy)Cl$_3$* in DMSO-*d$_6$* at 400 MHz at room temperature. The peak at 2.50 ppm is the residual solvent peak.

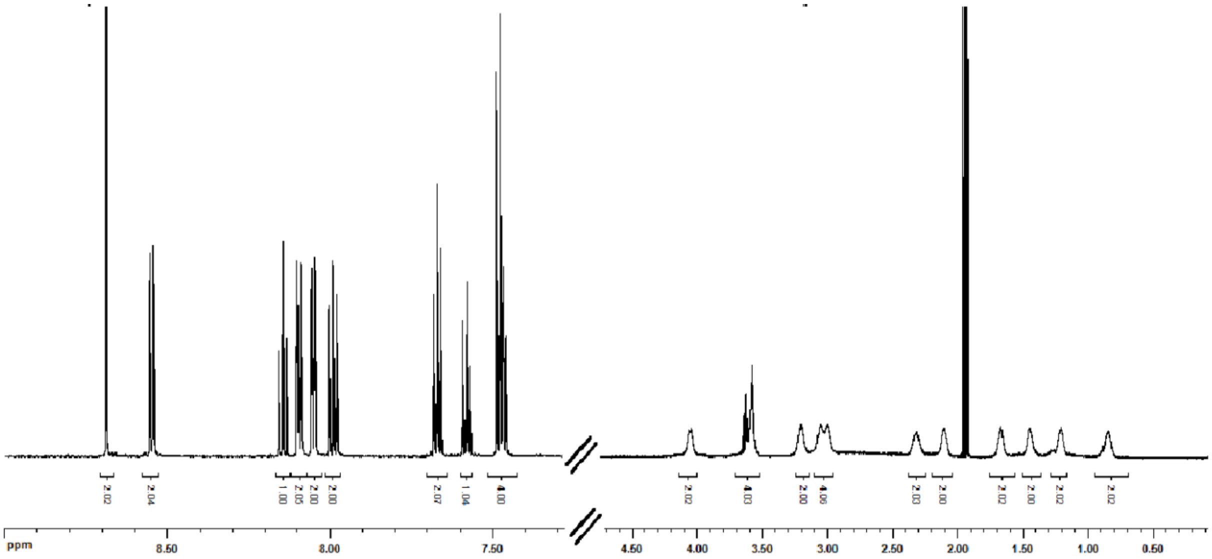


Figure S2. ^{1}H NMR of **1** in CD_3CN at 700 MHz at room temperature. The peak at 1.94 ppm is the residual solvent peak.

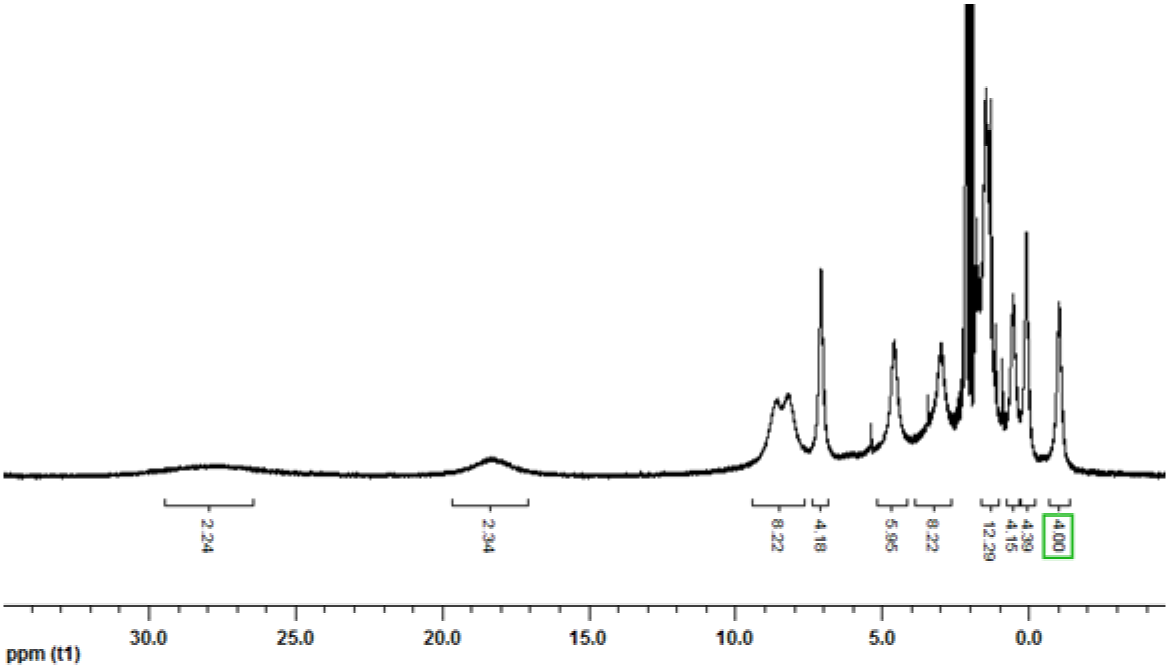


Figure S3. ^{1}H NMR of **2** in CD_3CN at 400 MHz at room temperature. The peak at 1.94 ppm is the residual solvent peak.

X-ray diffraction studies

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.[6] Absorption corrections were applied using SADABS.[7] Structures were solved by direct methods using SHELXS97 and refined on F^2 by full-matrix least squares using SHELXL97.[8] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropic on calculated positions using a riding model. For complex **1**, during the refinement of its structure, electron density peaks were located and were believed to be six severely disordered solvated acetone molecules (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,[9] which resulted in a significant improvement of R1 factor by ~3.5% in the squeezed structure. 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 to be due to the frequent discrete positional disorder of the freely rotating PF_6 anions. Several fluorine atoms were found to be positionally disordered, each of which were modelled as two components and refined anisotropically. Some atomic displacement restraints were applied among the disorder components to model the anion positions but not applicable for the cation structure.

For complex **2**, the highest difference peak is located 0.97 Å from atom F12B and the deepest hole is 0.36 Å from the atom F8, which are believed to be due to positional disorder arising from freely rotating PF_6 anions. One PF_6 anion was found with a significant degree of rotational disorder about the central P atom over two positions, with occupancy ratios [44:56] and [38:62] and both of them refined anisotropically. Some equivalent atomic displacement parameter (EADP) restraints were applied for few carbon atoms but not applicable for the entire cationic structure.

- **Additional discussion about crystallography**

The geometry optimized structures by DFT calculations of both **1** and **2** are in reasonable agreement with their respective X-ray structures (for a relative comparison of the bond distances and angles, as measured by X-ray data and DFT calculations for **1** and **2**, see Table S2). The Ru-N bond distance [1.946 (2) Å] to central pyridine ring of Ph-tpy is the shortest and the bond lengths closely resemble those observed in $[Ru(Ph\text{-}tpy)_2][PF_6]_2$.[10] As ligand **L1** is flexible, the **hpp** moietiesin complex **1** were found to be twisted from each other by 71.0(3)°. The average C-

N-C-N dihedral angle of 52.4(4)^o (average of <C40-N6-C22-N7 (49.9(4)^o and <C33-N8-C26-N7 (55.0(4)^o) indicates a broken π-conjugation between the pyridyl and the hpp units. Unlike the typical meridional heteroleptic Tpy-Ru^{II}-Tpy (where Tpy = substituted tpy) complexes, where the shortest Ru-N distances are (2.037(3)-2.043(3) Å) found between Ru-atom and the central py unit,[11] all the Ru-N distances in complex 2 are found to be similar (2.053(3)-2.074(4) Å).

Table S1. Crystallographic data of **1**·[6(C_3H_6O)] and **2**·[(C_3H_6O)].

Compound	**1**·[6(C_3H_6O)]	**2**·[C_3H_6O]
CCDC Number	978431	922650
Formula	[$C_{40}H_{42}N_{10}$Ru][PF_6]$_2$, [6(C_3H_6O)]	[$C_{38}H_{54}N_{14}$Ru][PF_6]$_3$, [C_3H_6O]
Mw (g/mol); $d_{\text{calcd.}}$(g/cm^3)	1402.31; 2.028	1301.01; 1.714
T (K); F(000)	100(2); 5808	100(2); 2652
Crystal System	Monoclinic	Orthorhombic
Space Group	C2/c	$P2_12_12_1$
Unit Cell:		
a (Å)	40.9186(5)	12.30660(10)
b (Å)	12.9990(2)	12.6126(2)
c (Å)	19.2466(2)	32.4825(4)
α (°)	90	90
β (°)	116.184(1)	90
γ (°)	90	90
V (Å^3); Z	9186.7(2); 8	5041.88(11); 4
θ range (°); completeness	2.41-70.71; 0.996	2.72-71.15; 0.997
R_{fle}:collec./indep.; R_{int}	177747/8737; 0.0265	67140/9381; 0.0296
μ (mm^{-1})	4.533	4.487
R1(F); wR(F^2); GoF(F^2)^a	0.0468; 0.1299; 1.038	0.0367; 0.0978; 1.025
Residual electron density	1.914; -0.777	1.196; -1.134

[a] R1(F) based on observed reflections with I>2σ(I) for **1**·[6(C_3H_6O)] and **2**·[C_3H_6O]; wR(F^2) and GoF(F^2) based on all data for all compounds.

Table S2. Selected bond distances and angles of **1**·[6(C_3H_6O)] and **2**·[(C_3H_6O)].

Compound	Bond Length			Angle		
1·[6(C_3H_6O)]		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·[(C_3H_6O)]	Ru1-N1	2.066(2)	2.11983	N1-Ru1-N4	83.47(10)	82.462
	Ru1-N4	2.053(3)	2.12115	N1-Ru1-N7	84.34(10)	82.526
	Ru1-N7	2.067(3)	2.11459	N4-Ru1-N7	92.17(10)	91.774
	Ru1-N8	2.062(2)	2.11984	N8-Ru1-N11	84.03(10)	82.525
	Ru1-N11	2.074(3)	2.11450	N8-Ru1-N14	82.60(10)	82.461
	Ru1-N14	2.071(3)	2.12122	N11-Ru1-N14	92.00(11)	91.772
				N1-Ru1-N14	178.14(10)	175.528
				N4-Ru1-N8	177.74(10)	175.532
				N7-Ru1-N11	171.04(10)	172.724

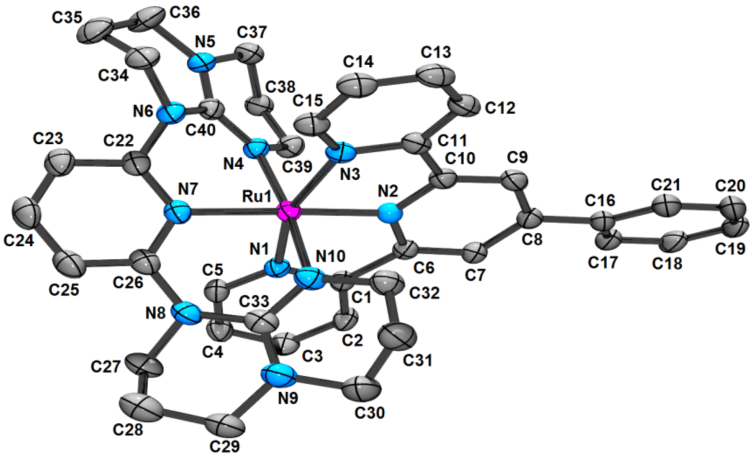


Figure S4. View of ORTEP diagram of **1** (ellipsoids correspond to a 50% probability level), with complete labeling. Hydrogen atoms, anions and solvent molecules are omitted for clarity.

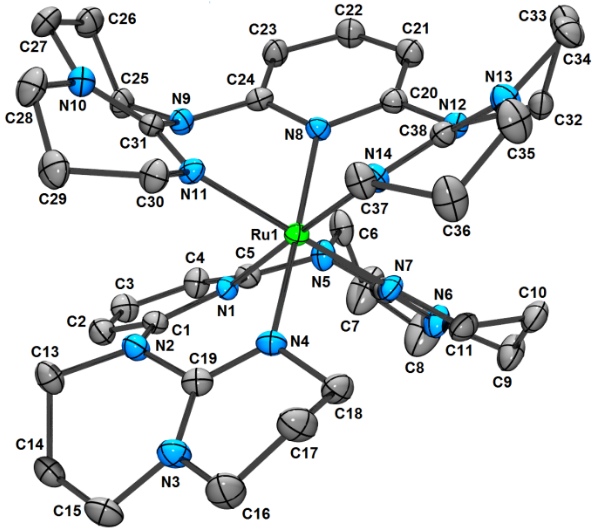


Figure S5. View of ORTEP diagram of **2** (ellipsoids correspond to a 50% probability level), with complete labeling. Hydrogen atoms, anions and solvent molecules are omitted for clarity.

- ## Electrochemical data

Table S3. Electrochemical data for **L1**, **1**, **2** and some reference compounds.

Compound	$E_{1/2}$(ox)[a]		$E_{1/2}$(red)[a]		$\Delta E_{1/2}$[b]
L1	1.11 (308)	0.77 (irr)[c]	------		------
1	------	0.50 (94)	-1.47 (70)	-2.01 (84)	1.97
2	1.18 (147)	------	-0.29 (138)		1.47
$[Ru(tpy)_2][(PF_6)_2]$[d]	1.31 (60)	------	-1.23 (70)	-1.47 (69)	2.54
$[Ru(Ph\text{-}tpy)_2]^{2+}$[e]	1.29	------	-1.26		2.55
$[Ru(tpy)(N\text{^}C\text{^}N)]^{+}$[f,g]	------	0.51 (62)	-1.55 (63)		2.06

[a] Potentials are in volts *vs.* SCE for acetonitrile solutions, 0.1 M in [*n*-Bu_4N]PF_6, recorded at 25 ± 1 °C at a sweep rate as mentioned in experimental section. The difference between cathodic and anodic peak potentials (millivolts) is given in parentheses. [b] Difference between the first oxidation and first reduction potentials (volt). [c] Irreversible; potential is given for the anodic wave. [d] From ref. 12. [e] From ref. 13. [f] From ref. 14. [g] N^C^N = 1,3-di(2-pyridyl)benzene.

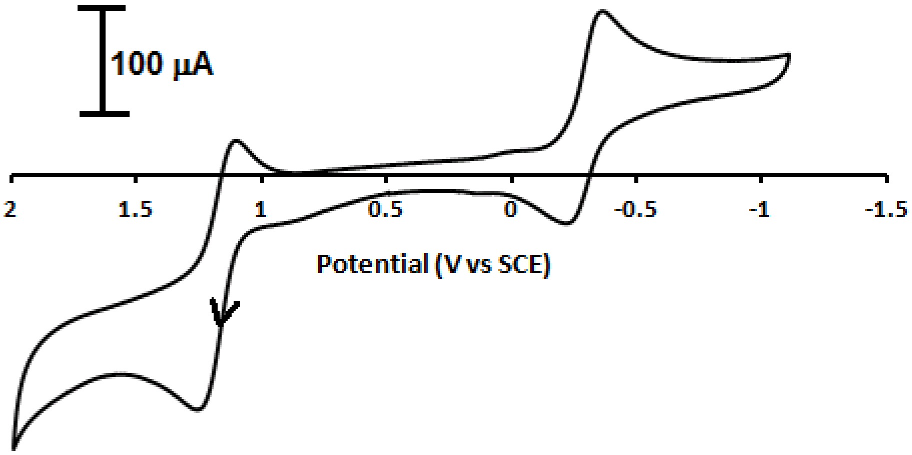


Figure S6. Cyclic voltammogram of **2** in dry, degassed CH_3CN, recorded at a scan rate of 25 mV/s.

- **DFT, TD-DFT calculations and UV-vis absorption and Emission data**

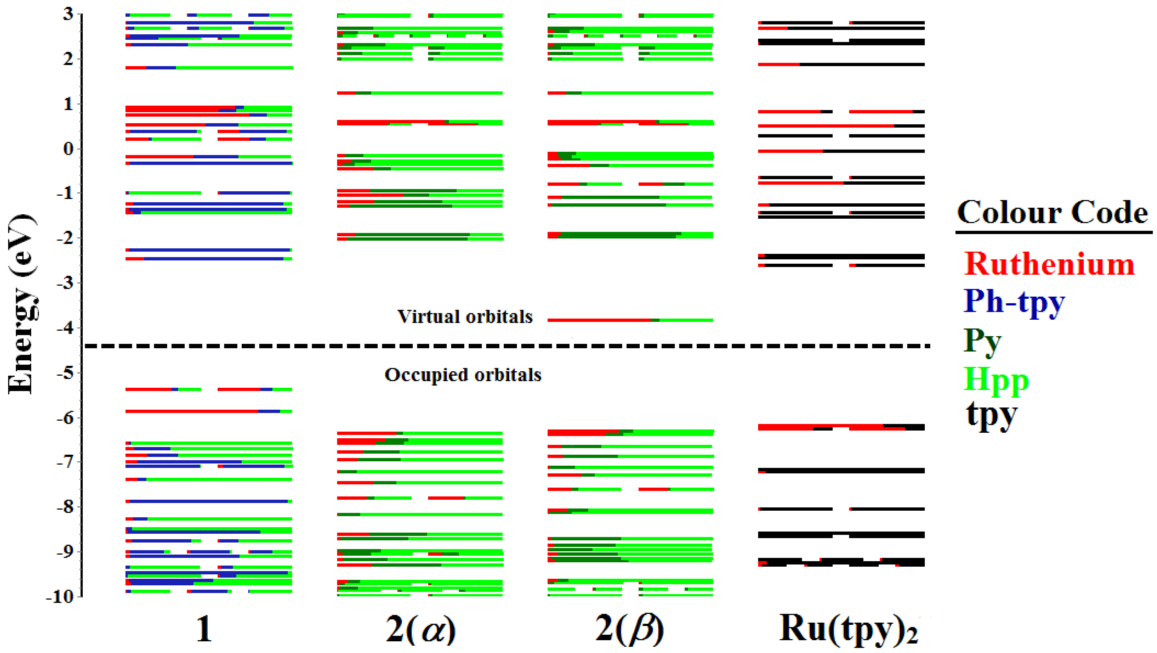


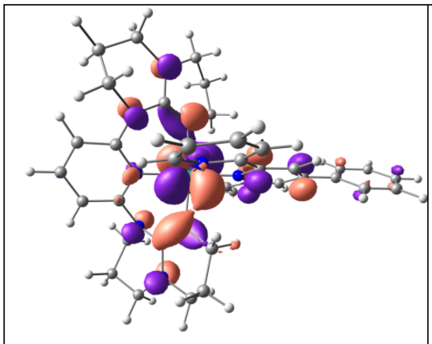
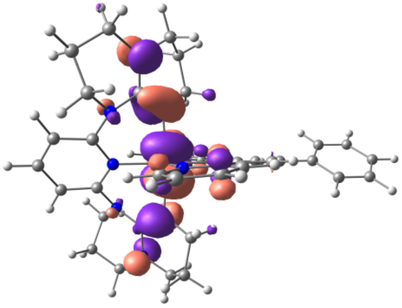
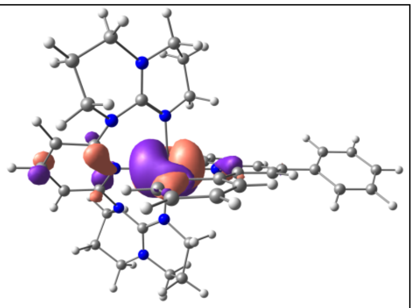
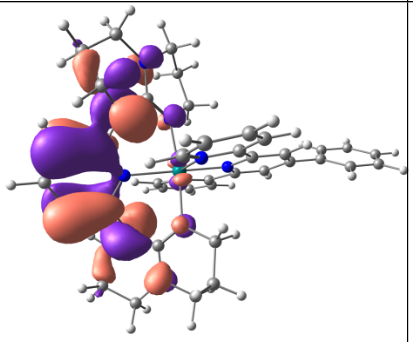
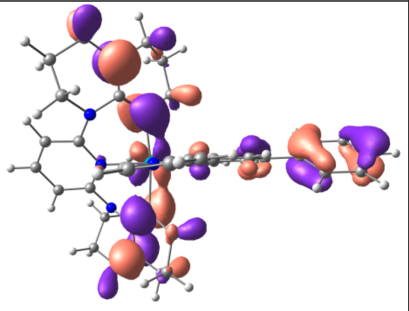
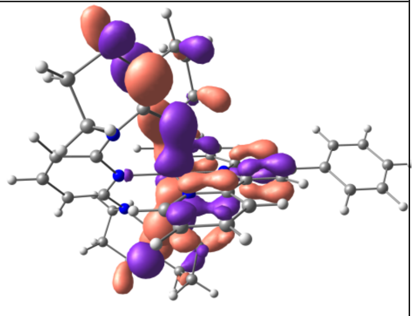
Figure S7. Calculated frontier MO energies of all the modeled **1**, **2** and Ru(tpy)$_2$ complexes obtained from DFT(b3lyp/LanL2DZ(f))[Ru]6-31G**[NCN] with CPCM(CH$_3$CN) and 0.05 eV of threshold of degeneracy. Restricted closed shell model was applied for diamagnetic complexes, **1** and Ru(tpy)$_2$, while unrestricted open shell model was applied for paramagnetic complex, **2**.

Table S4. MO composition of Ru(tpy)$_2^{2+}$ in singlet (*S*=0) ground state (rb3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N]).

MO	Energy (eV)	Approximate Composition (%)	
		Ru	tpy
LUMO+5	-1.44	1	99
LUMO+4	-1.53	0	100
LUMO+3	-2.37	3	97
LUMO+2	-2.44	0	100
LUMO+1	-2.60	7	93
LUMO	**-2.60**	**7**	**93**
HOMO	**-6.18**	**70**	**30**
HOMO-1	-6.25	72	28
HOMO-2	-6.26	72	28
HOMO-3	-7.16	0	100
HOMO-4	-7.21	3	97
HOMO-5	-8.03	2	98

Table S5. MO composition of **1**$^{2+}$ in singlet (S=0) ground state (rb3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N]).

MO	Energy (eV)	Approximate Composition (%)		
		Ru	Ph-tpy	**L1**
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
		
HOMO-3	HOMO-4	HOMO-5

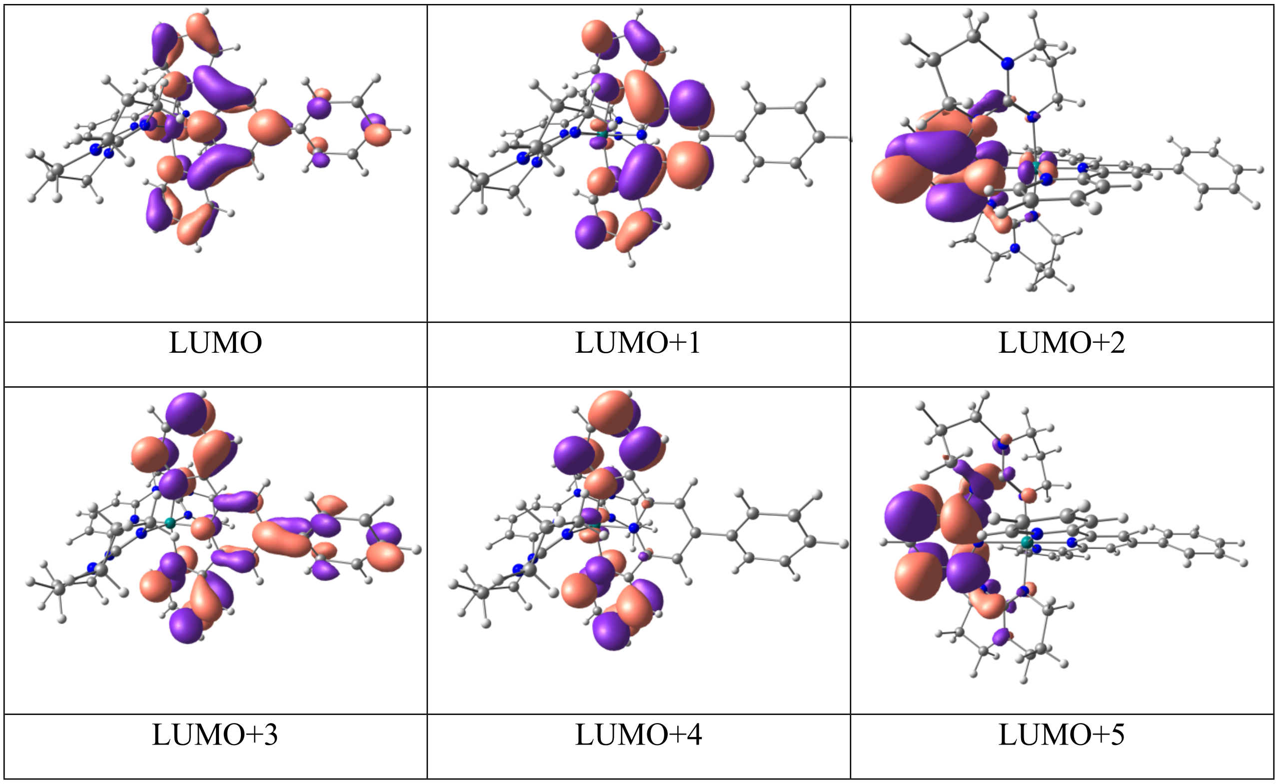

LUMO LUMO+1 LUMO+2
LUMO+3 LUMO+4 LUMO+5

Figure S8. Kohn-Sham electron density sketches in different MOs for $\mathbf{1}^{2+}$ in ($S=0$) ground state

Table S6. UV-vis absorption data of **L1**, **1**, **2** in dry degassed acetonitrile and some reference compounds.

Compound	λ_{max}, nm (ε x10^3, $M^{-1}cm^{-1}$)						
L1	228 (29.0)	311 (12.8)					
1	225 (26.2)	244 (22.6)	289(26.9)	317 (13.3)	379 (6.1)	541 (5.0)	622 (3.3)
2	234 (35.2)	326 (12.8)	433 (3.9)	564 (1.9)			
$Ru(tpy)_2^{2+a}$	270(40.9)	307(66.7)	475(15.3)				
$Ru(tpy)(N^\wedge C^\wedge N)^{+b}$	243(49.8)	277(47.0)	315(37.0)	368(sh)	424(9.6)	499(14.4)	

[a]From ref 15. [b]From ref 14.

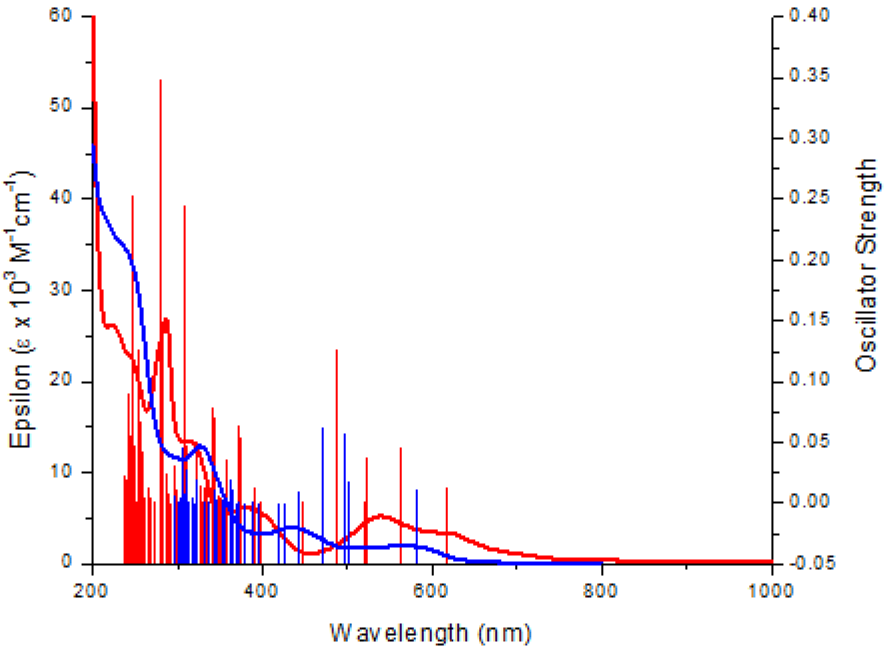


Figure S9. Overlay of experimental (curved lines) absorption spectra and calculated (straight lines) oscillator strengths at different wavelengths of **1** (red) and **2** (blue), at ambient temperature in dry acetonitrile.

Table S7. Selected transitions from TD-DFT calculations of **1**$^{2+}$ in the singlet ground state (rb3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N], CPCM (CH_3CN)).

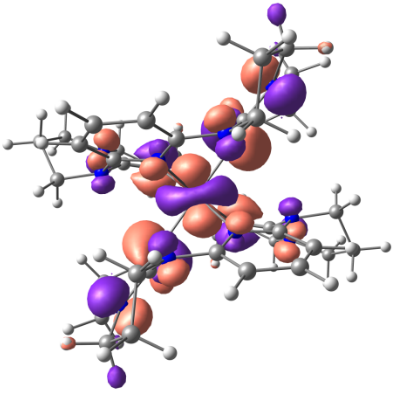
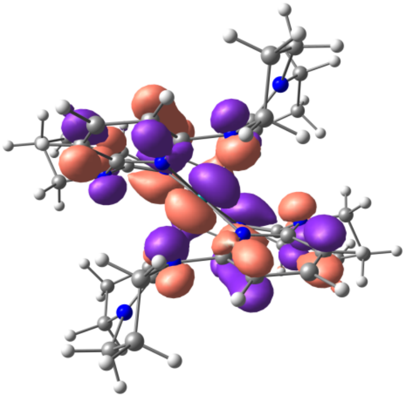
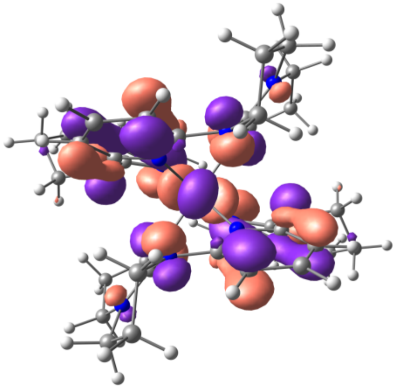
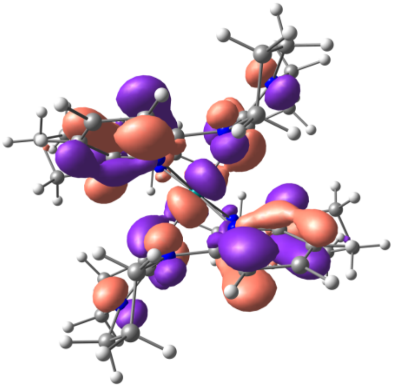
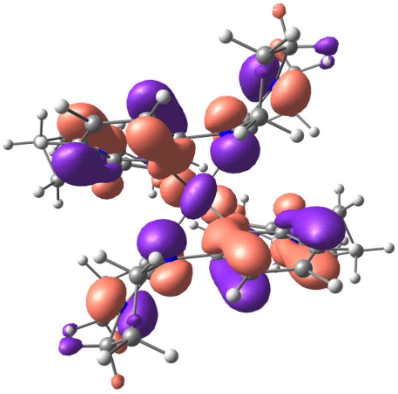
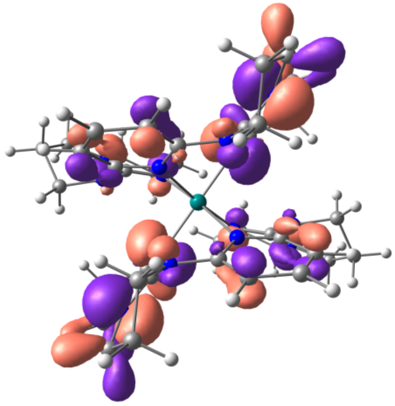
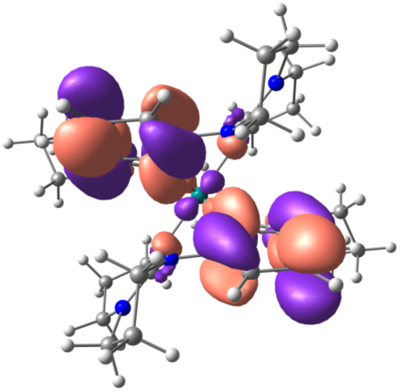
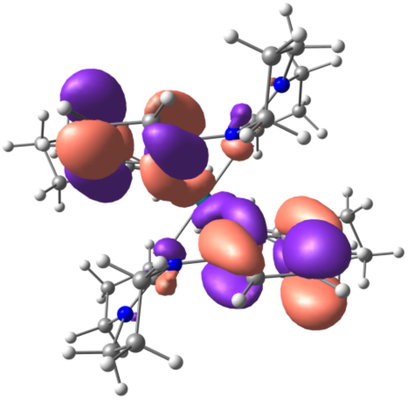
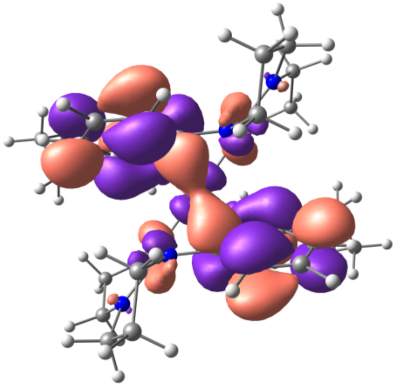
energy (eV)	λ/nm	λ/nm (εx10^3 M^{-1}cm^{-1}) [expt.]	f	transition	character
5.03	246	244(22.6)	0.2525	H-3->L+5 (68%)	hpp(π) to hpp(π*) &/or hpp(n) to hpp(π*)
4.44	279	289(26.9)	0.3477	H-7->L+1 (61%), H-8->L+1 (13%)	tpy(π) to tpy(π*)
4.02	308	317(13.3)	0.2449	H-7->L (51%)	tpy(π) to tpy(π*)
3.34	371	379(6.1)	0.0632	H-1->L+3 (92%)	Ru(dπ) to tpy(π*)
2.20	562	541(5.0)	0.0444	H->L (64%), H-1->L+1 (20%), H-2->L (10%)	Ru(dπ) to tpy(π*)
2.01	616	622(3.3)	0.0117	H-1->L (94%)	Ru(dπ) to tpy(π*)

Table S8. MO composition of $\mathbf{2}^{3+}$ in (S=1) ground state in α–spin (ub3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N]).

MO	Energy (eV)	Composition		
		Ru	Py	hpp
LUMO+5	-0.95	21	58	21
LUMO+4	-1.04	50	17	34
LUMO+3	-1.18	27	46	28
LUMO+2	-1.29	7	74	19
LUMO+1	-1.93	11	76	13
LUMO	**-2.02**	**5**	**82**	**13**
HOMO	**-6.35**	**31**	**3**	**65**
HOMO-1	-6.50	26	18	56
HOMO-2	-6.57	20	22	58
HOMO-3	-6.77	14	26	60
HOMO-4	-6.95	11	32	57
HOMO-5	-7.20	1	13	86

Table S9. MO composition of $\mathbf{2}^{3+}$ in (S=1) ground state in β–spin (ub3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N]).

MO	Energy (eV)	Composition		
		Ru	Py	hpp
LUMO+5	-0.82	56	9	34
LUMO+4	-1.09	9	68	24
LUMO+3	-1.27	2	80	18
LUMO+2	-1.89	8	80	12
LUMO+1	-1.97	6	81	14
LUMO	**-3.84**	**65**	**5**	**29**
HOMO	**-6.30**	**41**	**10**	**49**
HOMO-1	-6.39	33	13	55
HOMO-2	-6.66	8	28	64
HOMO-3	-6.87	8	40	52
HOMO-4	-7.11	1	18	81
HOMO-5	-7.28	20	8	72
HOMO-6	-7.59	38	2	60
HOMO-7	-7.61	32	10	58
HOMO-8	-8.07	13	11	75
HOMO-9	-8.12	1	15	84
HOMO-10	-8.70	0	51	49

		
HOMO	HOMO-1	HOMO-2
		
HOMO-3	HOMO-4	HOMO-5
		
LUMO	LUMO+1	LUMO+2

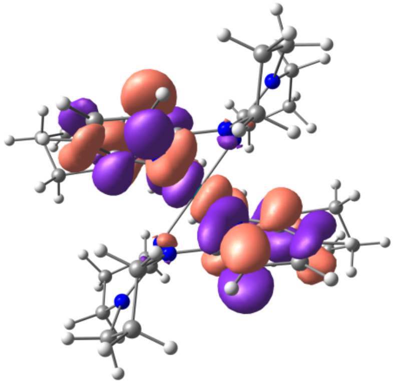
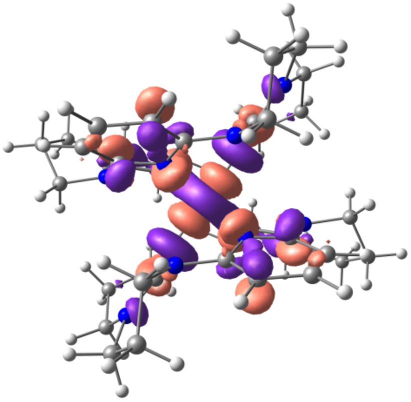
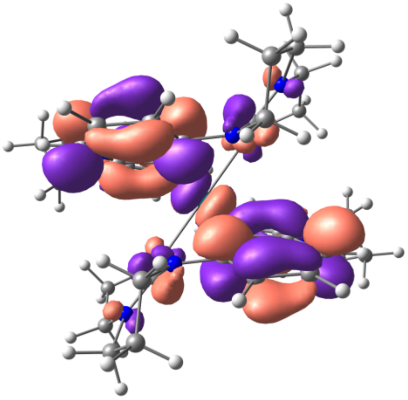
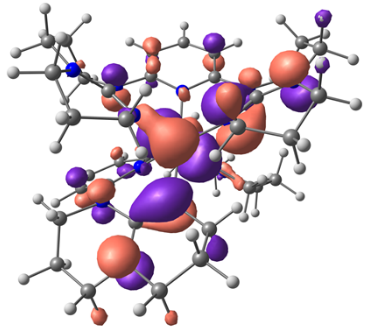
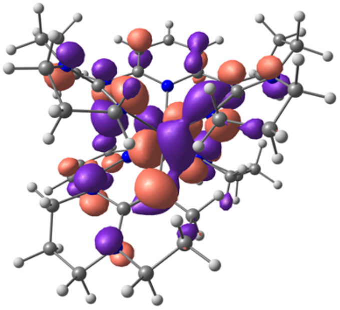
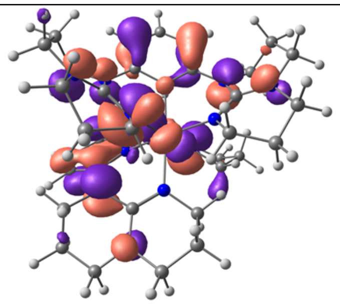
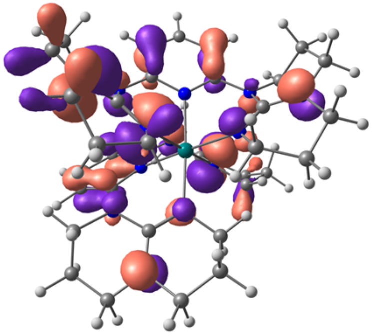
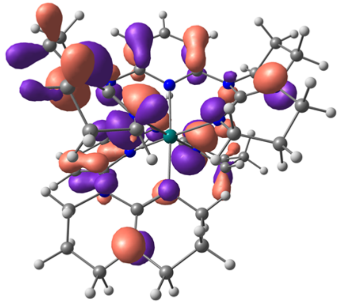
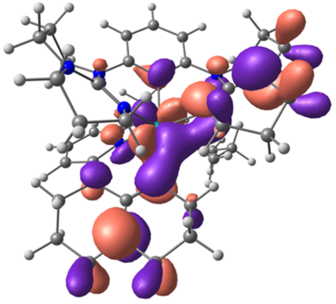
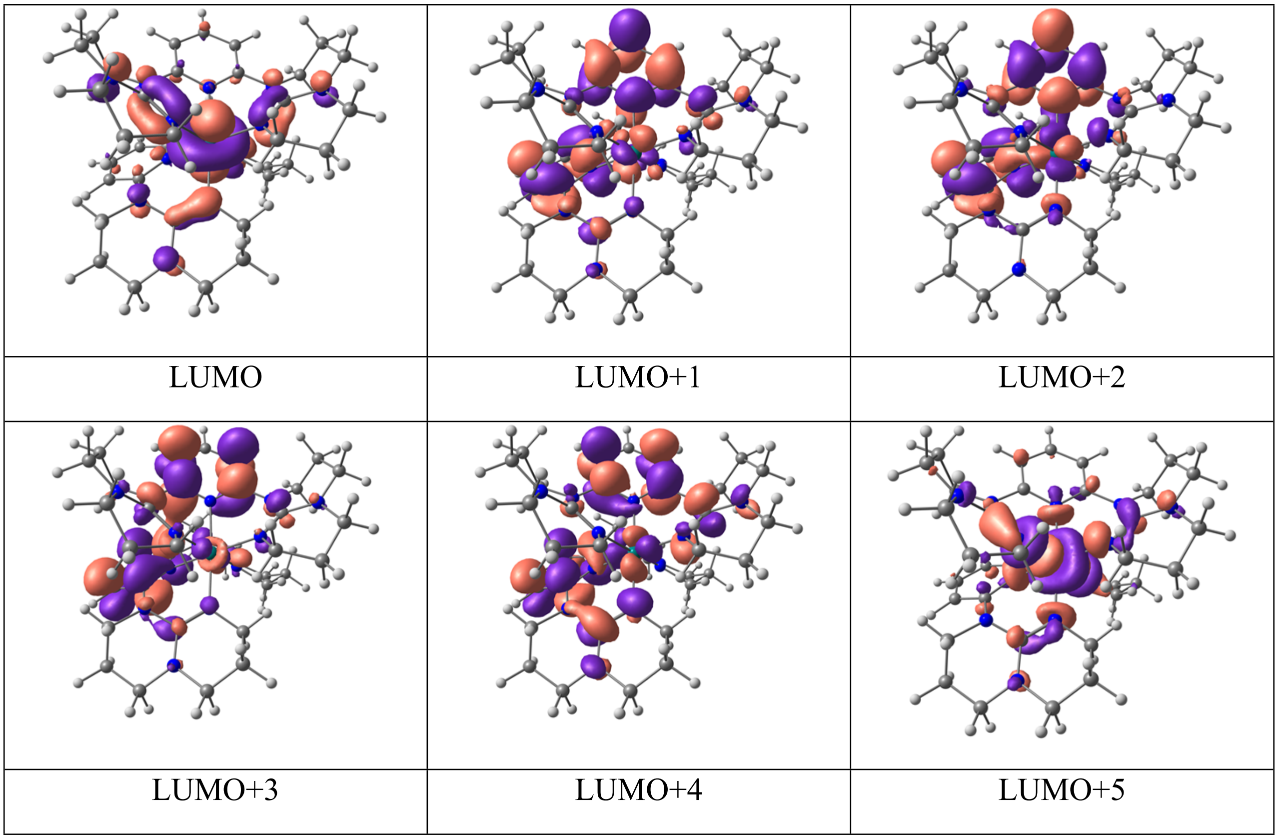
		
LUMO+3	LUMO+4	LUMO+5

Figure S10. Kohn-Sham electron density sketches of different MOs for $\mathbf{2}^{3+}$ in ($S=1$) ground state in α–spin

		
HOMO	HOMO-1	HOMO-2
		
HOMO-3	HOMO-4	HOMO-5



LUMO LUMO+1 LUMO+2

LUMO+3 LUMO+4 LUMO+5

Figure S11. Kohn-Sham electron density sketches of different MOs for $\mathbf{2}^{3+}$ in (S=1) ground state in β−spin

Table S10. Selected transitions from TD-DFT calculations of $\mathbf{2}^{3+}$ in the ground state (ub3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N], CPCM (CH_3CN)).

Energy (eV)	λ/nm	λ/nm (ε x 10^3 $M^{-1}cm^{-1}$) [expt.]	f	Major transition(s)	character
3.84	323	326 (12.8)	0.0116	H-10(β) -> L(β) (61%)	Py/hpp(n/π) to Ru(dπ) (major) + Py/hpp(n/π) to Py/hpp(π*)
2.64	469	433 (3.9)	0.0623	H-6(β) -> L(β) (81%)	hpp(n/π) to Ru(dπ) (major) + Ru(dπ) to hpp(π*) (minor)
2.13	581	564 (1.9)	0.0111	H-3(β) -> L(β) (59%), H-1(β) -> L(β) (23%), H-5(β) -> L(β) (12%)	Py/hpp(n/π) to Ru(dπ) (major) + Ru(dπ) to hpp(π*) (minor)

Table S11. Emission data of **L1** and **1**, **2** in dry degassed acetonitrile and some reference compounds.

Compound	Excited at λ_{max}, nm	Luminescence at 298 K		
		λ_{max}, nm	τ, ns	Φ (x 10^{-6})
L1	228, 311	360		
1	622, 541	**901**	**129**	**1000**
2	564, 433	------	------	------
Ru(tpy)$_2^{2+a}$	475	629	0.25	< 5
Ru(Ph-tpy)$_2^{2+a}$	488	715	1.0	40
Ru(tpy)(N^C^N)$^{+b}$	499	781	------	9.4

[a]From ref 13 (using Ru(bpy)$_3$(PF$_6$)$_2$ (Φ = 0.028) as standard). [b]From ref 14 (using Ru(bpy)$_3$(PF$_6$)$_2$ (Φ = 0.062) as standard).

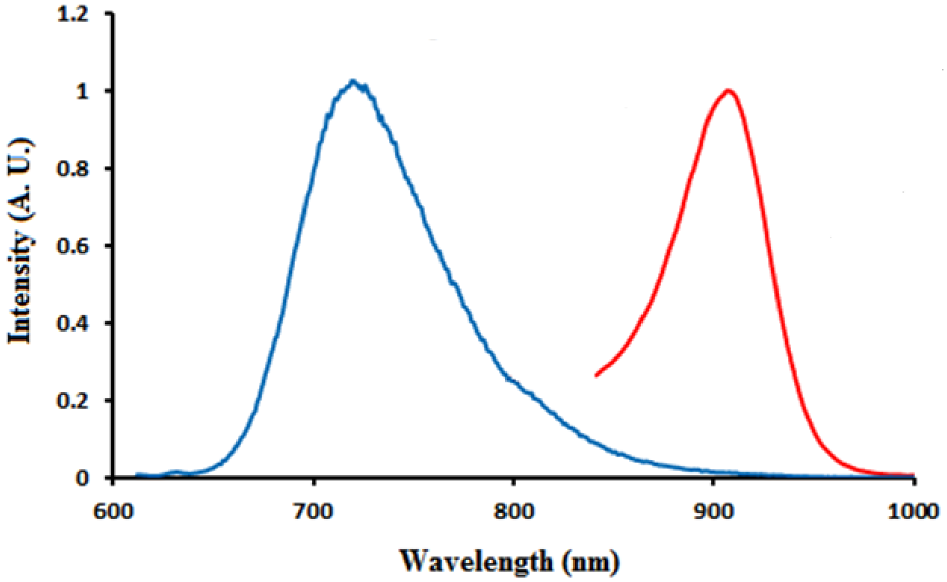


Figure S12. Emission spectra of complexes [Ru(Ph-tpy)$_2$][(PF$_6$)$_2$] (blue) and **1** (red), corrected for photomultiplier response.

- **Additional DFT data**

Computational details:

All calculations were performed with the Gaussian03[16] employing the DFT method, the Becke three-parameter hybrid functional,[17] and Lee-Yang-Parr's gradient-corrected correlation functional (B3LYP).[18] Singlet ground state geometry optimizations for $\mathbf{1}^{2+}$ and $\mathbf{2}^{3+}$ were carried out at the (R)B3LYP and (U)B3LYP levels, respectively, in the gas phase, using their respective crystallographic structures as starting points. All elements except Ru were assigned the 6-31G(d,f) basis set.[19] The double-ζ quality LANL2DZ ECP basis set[20] with an effective core potential and one additional f-type polarization was employed for the Ru atom. Vertical electronic excitations based on (R)B3LYP and (U)B3LYP-optimized geometries were computed for $\mathbf{1}^{2+}$ and $\mathbf{2}^{3+}$ using the TD-DFT formalism,[21a,b] respectively, in acetonitrile using conductor-like polarizable continuum model (CPCM).[22a-c] Vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and there are only positive eigenvalues. The electronic distribution and localization of the singlet excited states were visualized using the electron density difference maps (ED-DMs).[23] Gausssum 2.2 and Chemissian were employed to visualize the absorption spectra (simulated with Gaussian distribution with a full-width at half maximum (fwhm) set to 3000 cm-1) and to calculate the fractional contributions of various groups to each molecular orbital. All calculated structures and Kohn-Sham orbitals were visualized with ChemCraft.[24]

Table S12. Optimized Atomic coordinates obtained from DFT for **1^{2+}** in singlet ground state (rb3lyp/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

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   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
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Table S13. Optimized Atomic coordinates obtained from DFT for **2**$^{3+}$ in ground state (ub3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N]).

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---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
    1         44           0       -0.002715    0.399660   -0.013711
    2          7           0       -1.165717   -0.946667    1.036428
    3          7           0       -3.082467    0.407767    0.752916
    4          7           0       -3.289103    2.537075    1.656897
    5          7           0       -1.185491    1.791633    0.923749
    6          7           0        0.796241   -2.046974    1.675821
    7          7           0        2.195813   -1.132409    3.279170
    8          7           0        1.263223    0.262285    1.615081
    9          7           0        1.153897   -0.974733   -1.026198
   10          7           0       -0.815465   -2.093801   -1.621427
   11          7           0       -2.276328   -1.245576   -3.216340
   12          7           0       -1.267483    0.211105   -1.646255
   13          7           0        3.070494    0.361534   -0.730656
   14          7           0        3.340513    2.458310   -1.710168
   15          7           0        1.203213    1.753173   -1.015055
   16          6           0       -2.516779   -0.839736    1.061246
   17          6           0       -3.316456   -1.939703    1.361833
   18          1           0       -4.264419   -1.867831    1.355937
   19          6           0       -2.701879   -3.141409    1.667354
   20          1           0       -3.229716   -3.921205    1.800350
   21          6           0       -1.327468   -3.216602    1.780275
   22          1           0       -0.901398   -4.026477    2.037635
   23          6           0       -0.588628   -2.075913    1.505784
   24          6           0        1.524776   -3.305370    1.904047
   25          1           0        2.424070   -3.249982    1.494837
   26          1           0        1.037064   -4.055978    1.478595
   27          6           0        1.656483   -3.561228    3.398871
   28          1           0        0.767064   -3.762067    3.784968
   29          1           0        2.247748   -4.340574    3.556216
   30          6           0        2.215613   -2.378151    4.040125
   31          1           0        3.156566   -2.576442    4.277198
   32          1           0        1.724240   -2.228530    4.886123
   33          6           0        3.044080   -0.083264    3.849462
   34          1           0        3.898192   -0.474942    4.160925
   35          1           0        2.590236    0.329362    4.626629
   36          6           0        3.315998    0.969188    2.793226
   37          1           0        3.893958    0.596321    2.080421
   38          1           0        3.777293    1.746145    3.196033
   39          6           0        1.977787    1.396277    2.212356
   40          1           0        1.421333    1.794211    2.927535
   41          1           0        2.126525    2.090804    1.521756
   42          6           0        1.423934   -0.904340    2.206707
   43          6           0       -4.547032    0.490401    0.624124
   44          1           0       -4.914279   -0.382783    0.334854
   45          1           0       -4.792851    1.173291   -0.049778
   46          6           0       -5.107487    0.871754    1.985420
   47          1           0       -4.789041    0.242874    2.680633
```

48	1	0	-6.097954	0.852975	1.971540
49	6	0	-4.600932	2.280609	2.260501
50	1	0	-5.253102	2.933702	1.904878
51	1	0	-4.537787	2.417516	3.239671
52	6	0	-2.887439	3.946965	1.807329
53	1	0	-2.790902	4.163369	2.767894
54	1	0	-3.588480	4.533355	1.427234
55	6	0	-1.587827	4.196080	1.104187
56	1	0	-1.199763	5.059268	1.400576
57	1	0	-1.732120	4.237630	0.125379
58	6	0	-0.640683	3.050758	1.445224
59	1	0	0.248271	3.221592	1.046055
60	1	0	-0.532396	2.987725	2.427683
61	6	0	-2.472199	1.604164	1.146744
62	6	0	2.511618	-0.883604	-1.025443
63	6	0	3.301219	-1.987160	-1.289542
64	1	0	4.249684	-1.920889	-1.265425
65	6	0	2.694820	-3.181678	-1.585813
66	1	0	3.223883	-3.962722	-1.696489
67	6	0	1.320976	-3.260216	-1.725680
68	1	0	0.900355	-4.069021	-1.986946
69	6	0	0.579040	-2.114429	-1.469318
70	6	0	-1.500820	-3.386315	-1.853270
71	1	0	-2.422367	-3.352244	-1.491903
72	1	0	-1.012821	-4.115695	-1.394616
73	6	0	-1.537823	-3.643851	-3.345046
74	1	0	-1.966092	-4.517194	-3.533862
75	1	0	-0.619036	-3.657579	-3.713578
76	6	0	-2.345825	-2.508958	-3.972492
77	1	0	-2.012563	-2.349457	-4.891269
78	1	0	-3.292554	-2.788594	-4.038583
79	6	0	-3.147589	-0.204924	-3.784509
80	1	0	-4.020212	-0.602929	-4.032619
81	1	0	-2.732654	0.162765	-4.604386
82	6	0	-3.363629	0.898087	-2.792837
83	1	0	-3.932721	0.578885	-2.048945
84	1	0	-3.817822	1.661615	-3.229683
85	6	0	-2.003079	1.336148	-2.258490
86	1	0	-1.467002	1.712771	-3.000805
87	1	0	-2.131348	2.048102	-1.583691
88	6	0	-1.468029	-0.979148	-2.180709
89	6	0	4.535934	0.451683	-0.535131
90	1	0	4.886105	-0.409380	-0.190113
91	1	0	4.747233	1.161766	0.122062
92	6	0	5.172698	0.773138	-1.871302
93	1	0	4.893993	0.113872	-2.554450
94	1	0	6.159466	0.756284	-1.797309
95	6	0	4.692533	2.161621	-2.247531
96	1	0	5.332862	2.832925	-1.901601
97	1	0	4.673129	2.240418	-3.235302
98	6	0	2.951583	3.844781	-1.954897
99	1	0	2.904109	4.006091	-2.930414
100	1	0	3.638186	4.451727	-1.576796
101	6	0	1.613615	4.150265	-1.328231

```
 102           1             0        1.242465    4.984657   -1.708109
 103           1             0        1.715327    4.269646   -0.350380
 104           6             0        0.683750    2.990582   -1.616799
 105           1             0       -0.214191    3.185233   -1.249838
 106           1             0        0.596465    2.871061   -2.596302
 107           6             0        2.498457    1.555243   -1.183595
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