Electronic Supplementary Material (ESI) for Dalton Transactions.

Stereoselective formation of a *meso*-diruthenium(II,II) complex and tuning the properties of its monoruthenium analogues

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Supporting Information

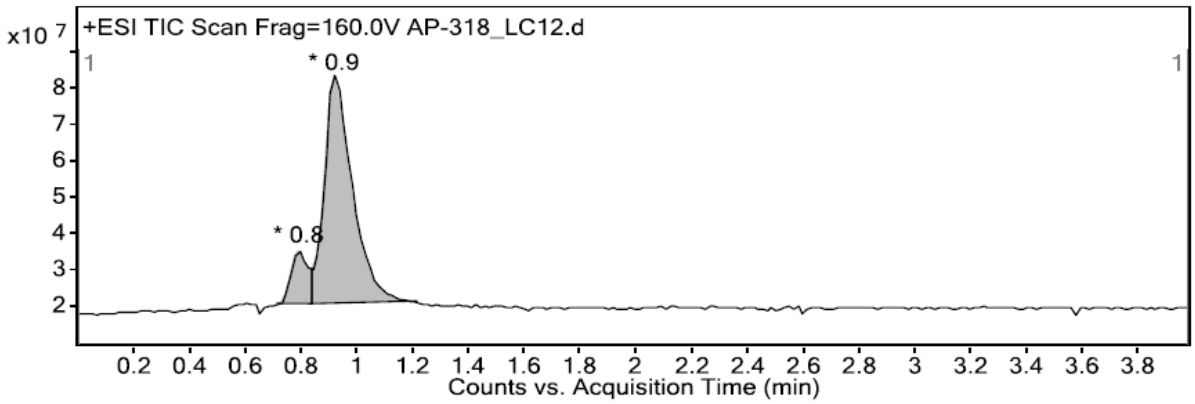
Materials, methods and instrumentation

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 (1.24 ppm for CD_3CN, 77.00 ppm for $CDCl_3$) of the solvent.

All the photophysical measurements were carried out in deaerated acetonitrile at r.t. in septa-sealed quartz cells. Absorption spectra were measured on a Cary 500i UV-Vis-NIR Spectrophotometer. For luminescence spectra a Cary Eclipse Fluorescence spectrofluorimeter was used. 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). Luminescence quantum yields have been performed by the optical dilute method.[1] As quantum yield reference, $[Ru(bpy)_3]^{2+}$ in aqueous deaerated solution was used ($\Phi = 0.095$).[2] For each sample, linear least-squares fit of values were obtained from at least three independent solutions at varying concentrations with emission intensity. 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 of **L1**, **1**-***meso*** and **2**-**4** were obtained at scan rates of 100, 25 and 50 mV/s, 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 mVs−1 and a pulse amplitude, width and period of 50 mV, 50 ms and 200 ms, respectively.

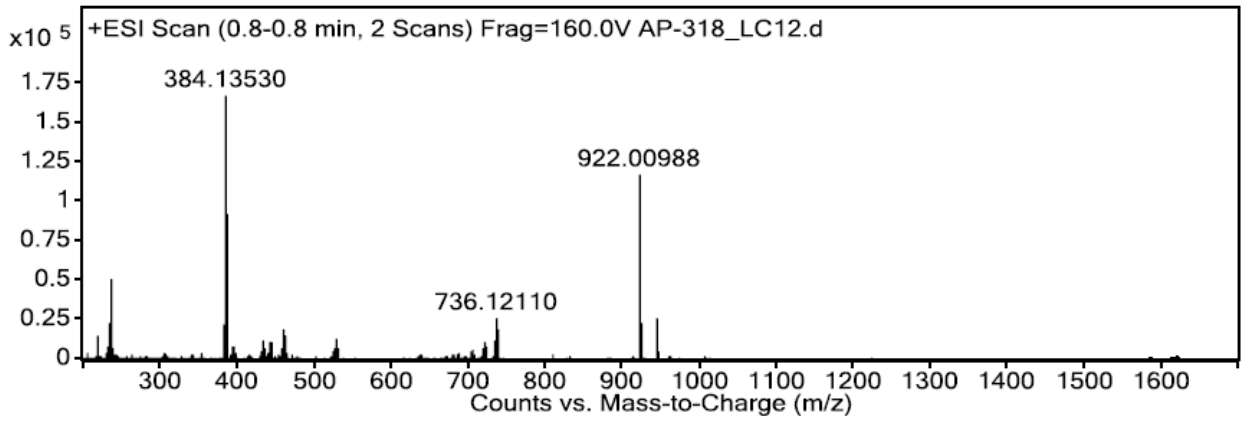
Experimental uncertainties are as follows: absorption maxima, ±2 nm; molar absorption coefficient, 10%; redox potentials, ± 10 mV, emission maxima, ±2 nm, emission lifetimes, ± 10%.

1,3,4,6,7,8-Hexahydro-2*H*-pyrimido[1,2-α]pyrimidine (**H-hpp**), 4,6-dichloropyrimidine, $AgNO_3$, and KPF_6 were purchased from Aldrich as used as received. *Cis*-$Ru(bpy)_2Cl_2$.$2H_2O$ was synthesized using literature procedure.[3]



Integration Peak List

RT	Height	Area
0.8	14722971	68546361
0.9	62945285	443168110



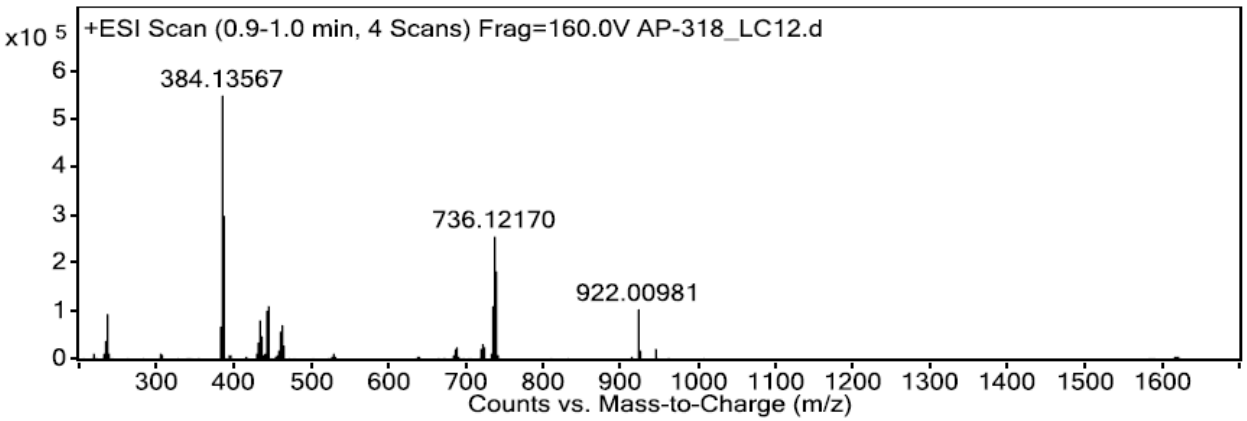


Figure S1. LC-MS of reaction ii (see Scheme **1** in main text) using an achiral support, showing the separation of the *rac*-ΔΔ or ΛΛ-isomer (retention time at 0.8 min) and the *meso*-ΔΛ or ΛΔ-isomer (retention time at 0.9-1.0 min) (Figure adopted from ref 4).

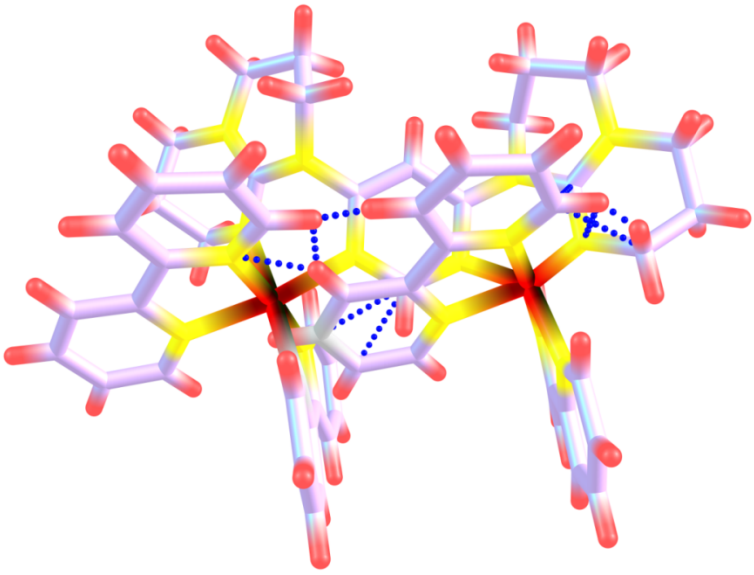


Figure S2. View of capped stick model of *rac*-ΛΛ or ΔΔ-diastereomer, as the initial coordinates for DFT calculation, sketched using Chemcraft. The blue dots show the severe steric interactions between the colliding atoms.

X-ray diffraction studies

Single crystals of **1-*meso***, suitable for X-ray structure determination, were grown by slow vapour diffusion of diethyl ether into concentrated acetonitrile solution of **1-*meso***. Diffraction data were collected on a Bruker SMART 6000 with Montel 200 monochromator, equipped with a rotating anode source for Cu Kα radiation. 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 the crystal structure of **1-*meso***, the highest difference peak is located 1.24 Å from atom Ru1. In addition, in **1-*meso*** three more peaks with density around 1 e/Å^3 were present essentially 1.25 Å from Ru-atoms. The other Q peak of 0.81 e/Å^3 is due to rotational disorder of fluorine atom F12, and this small disorder was not taken into account for modelling. Similarly for complexes **3** and **4**, these first two and first three high Q

peaks, respectively, are in close proximity to Ru-atoms (~ 0.91 Å from Ru1 in **3** and 0.79-0.90 Å from Ru1 in **4**). For complex **3**, two other Q peaks of 1.53 e/Å^3 and 1.26 e/Å^3 were located near to F-atoms. These Q peaks were believed to arise from the positional disorder of F-atoms, which were not taken into consideration for modelling. In complex **4**, atom C29 in the cationic moiety was found to be disordered over two positions and the disorder was modelled with occupancy ratios [44:56] and then refined anisotropically. One 'fixed distance' (DFIX) restraint was applied to the C28-H28A distance in complex **4**, for otherwise freely floating H28A atom, but nowhere else applicable to the rest of the cationic structure. The diffraction quality of the crystal of complex **2** was checked, revealing poor diffraction with a large amount of diffuse scattering, signaling extensive crystal disorder. For this compound, during the refinement of its structure, electron density peaks were located and were believed to be eight highly 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,[8] which resulted in a significant improvement of R1 factor by ~ 4%. The two high Q peaks of 1.22 e/Å^3 and 1.06 e/Å^3 were essentially due to the positional disorder of F-atoms in freely rotating PF_6 anion, and this disorder was not taken into consideration for modelling.

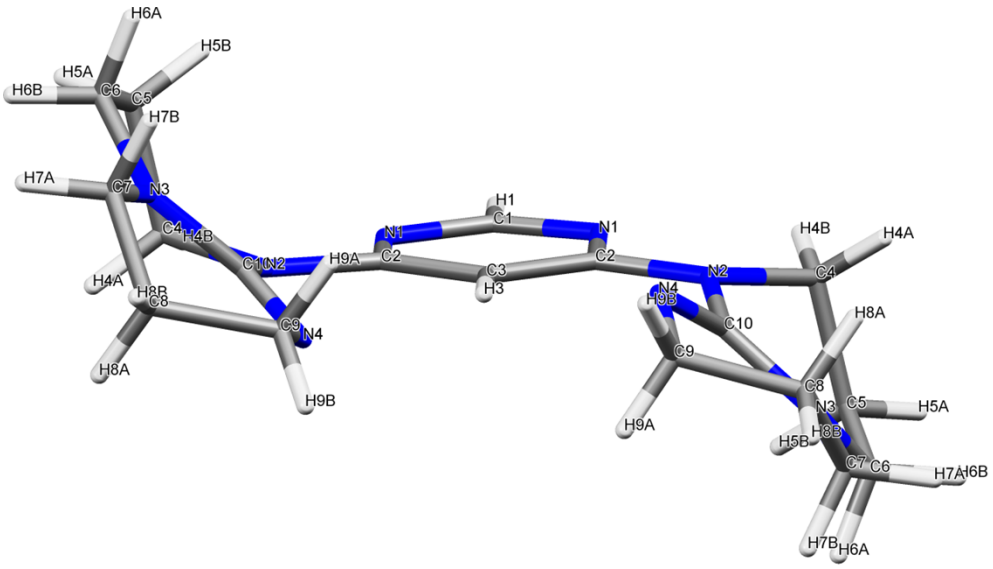


Figure S3. View of capped stick model of **L1**, along the plane consisting of pyrimidine, showing the chair conformation of **L1**. The pyrimidine ring is twisted with respect to the **hpp** units to minimize the lone pair-lone pair interactions on the hetero atoms.

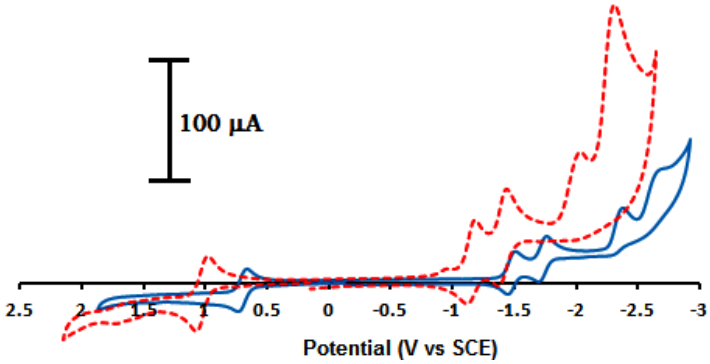
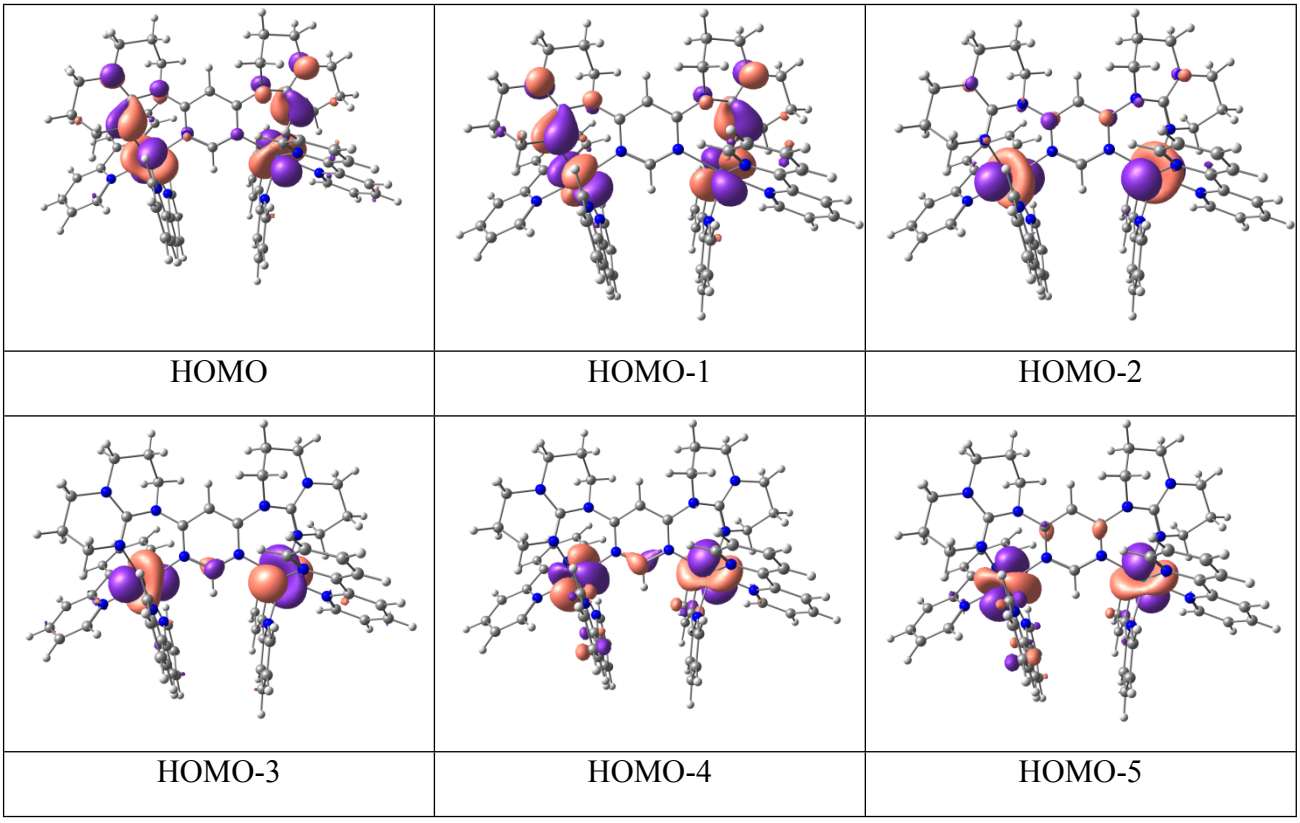


Figure S4. Cyclic voltammogram of **3** (blue, bold line) and **4** (red, dotted line) in dry, degassed CH_3CN, recorded at a scan rate of 50 mV/s.

DFT Calculations:

Table S1. MO Composition of **1-*meso*** $^{4+}$ in Singlet (*S*=0) Ground State (b3lyp/LanL2DZ(f)[Ru]6−31G**[C,H,N]).

MO	Energy (eV)	Composition			
		Ru	BPy	Pyrimidine	Hpp
LUMO+6	-1.82	4	95	1	1
LUMO+5	-2.35	4	13	79	5
LUMO+4	-2.59	4	8	73	15
LUMO+3	-2.61	6	92	2	0
LUMO+2	-2.64	5	85	8	2
LUMO+1	-2.71	2	96	1	1
LUMO	**-2.72**	**2**	**92**	**4**	**2**
HOMO	**-5.94**	**60**	**12**	**2**	**26**
HOMO-1	-5.99	57	12	1	30
HOMO-2	-6.26	82	11	3	4
HOMO-3	-6.30	85	12	2	1
HOMO-4	-6.50	82	14	3	1
HOMO-5	-6.52	82	15	2	1



HOMO | HOMO-1 | HOMO-2

HOMO-3 | HOMO-4 | HOMO-5

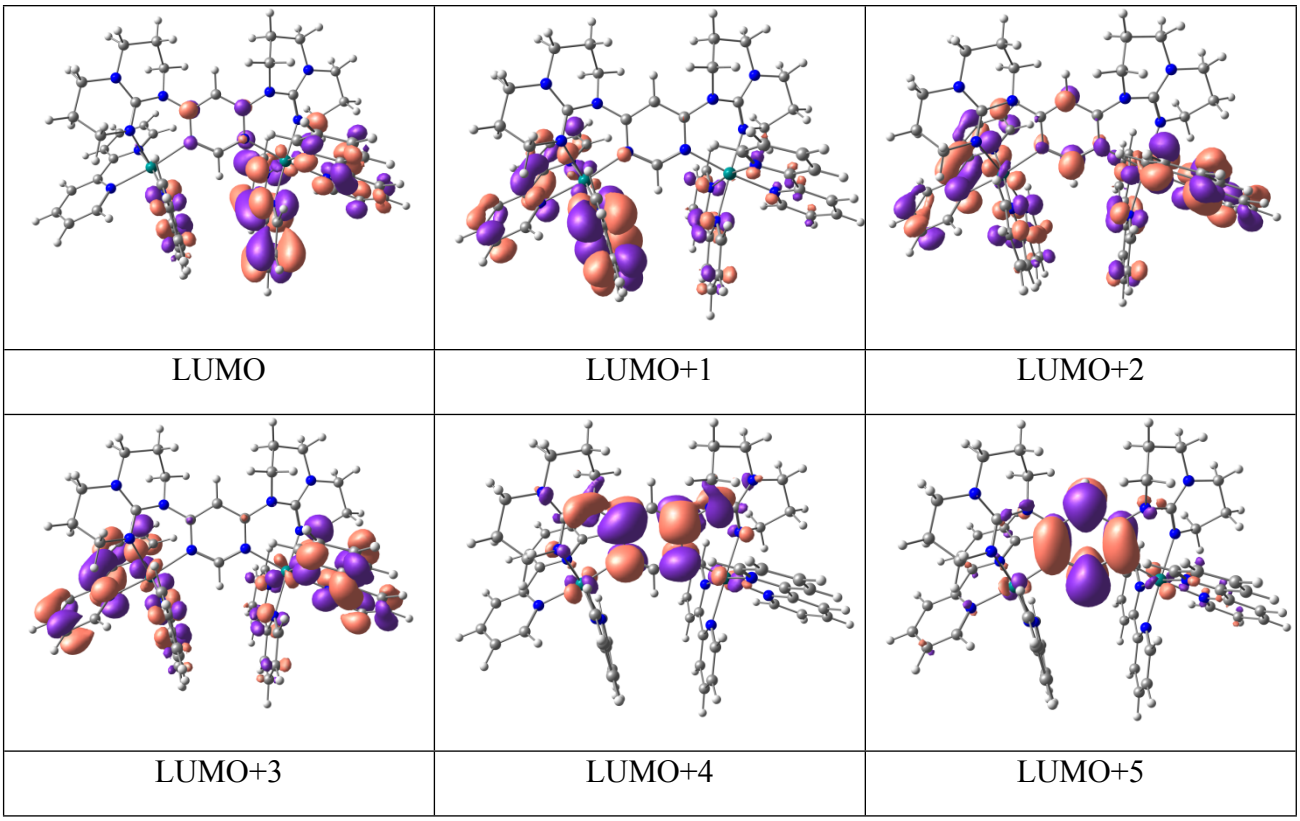


Figure S5. Kohn-Sham molecular orbital sketches for **1(*meso*)**$^{4+}$ in (*S=0*) ground state

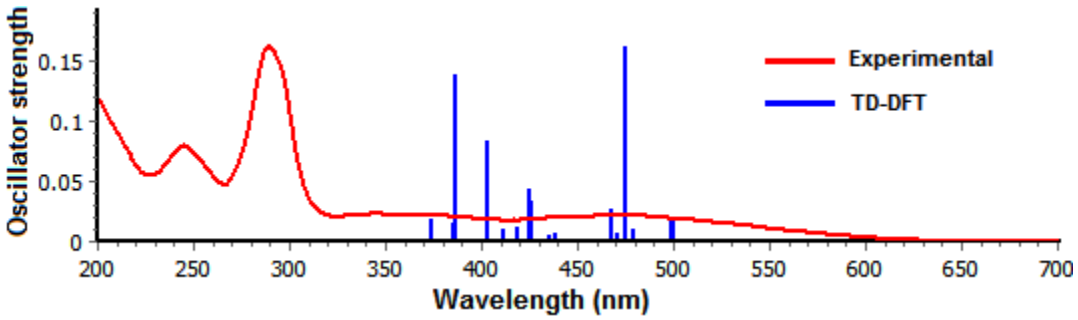


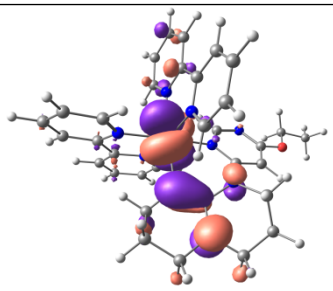
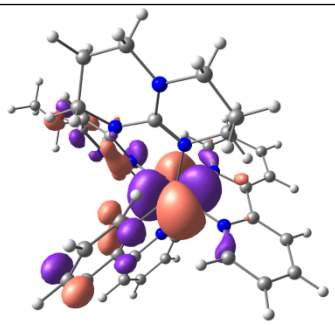
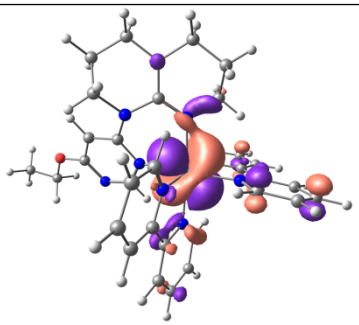
Figure S6. Overlap of experimental electronic absorption spectra with oscillator strength from TD-DFT calculation of **1(*meso*)**$^{4+}$ in (*S=0*) ground state. Due to memory allocation problem only the first thirty transitions were calculated.

Table S2. Selected Transitions from TD-DFT calculations of **1-*meso*$^{4+}$** in the Singlet Ground State (b3lyp/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
3.22	384	368 (7.0)	0.1385	H-4->L+4 (52%)	Ru(dπ) to Pyrimidine(π*)
2.62	473	470 (6.8)	0.1615	H->L+2 (52%), H-1->L+3 (25%)	Ru(dπ) to Bpy(π*) (major) + hpp(n/π) to Bpy(π*) (minor)
2.49	498	511 (5.6)	0.0198	H-1->L+1 (32%), H->L (38%), H->L+1 (17%)	Ru(dπ) to Bpy(π*) (major) + hpp(n/π) to Bpy(π*) (minor)

Table S3. MO Composition of **2**$^{2+}$ in Singlet (*S*=0) Ground State (b3lyp/LanL2DZ(f)[Ru]6−31G**[C,H,N,O]).

MO	Energy (eV)	Composition				
		Ru	BPy	Pyrimidine	Hpp	Adduct (OEt)
LUMO+6	-1.25	2	68	25	2	2
LUMO+5	-1.36	2	53	37	5	3
LUMO+4	-1.38	3	75	20	1	2
LUMO+3	-1.48	2	50	46	2	0
LUMO+2	-1.62	2	83	14	1	0
LUMO+1	-2.39	6	93	1	0	0
LUMO	**-2.45**	**3**	**97**	**0**	**0**	**0**
HOMO	**-5.58**	**63**	**10**	**1**	**26**	**0**
HOMO-1	-6.01	79	13	6	1	1
HOMO-2	-6.08	80	16	1	3	0
HOMO-3	-7.03	18	8	10	61	3
HOMO-4	-7.13	1	12	27	55	5
HOMO-5	-7.26	1	96	2	1	1
HOMO-6	-7.29	1	89	2	6	1

		
HOMO	HOMO-1	HOMO-2

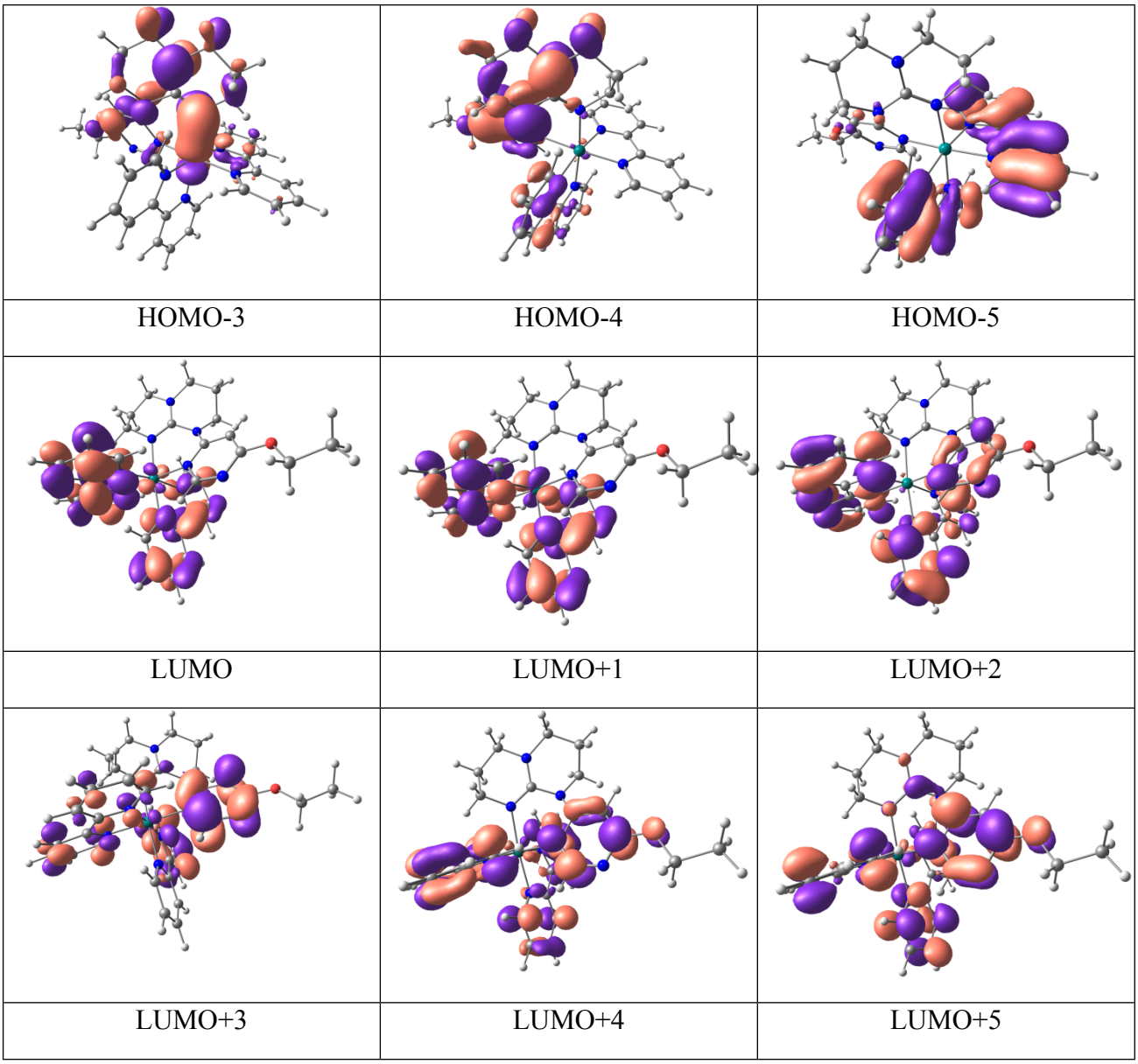


Figure S7. Kohn-Sham molecular orbital sketches for $\mathbf{2}^{2+}$ in (*S=0*) ground state

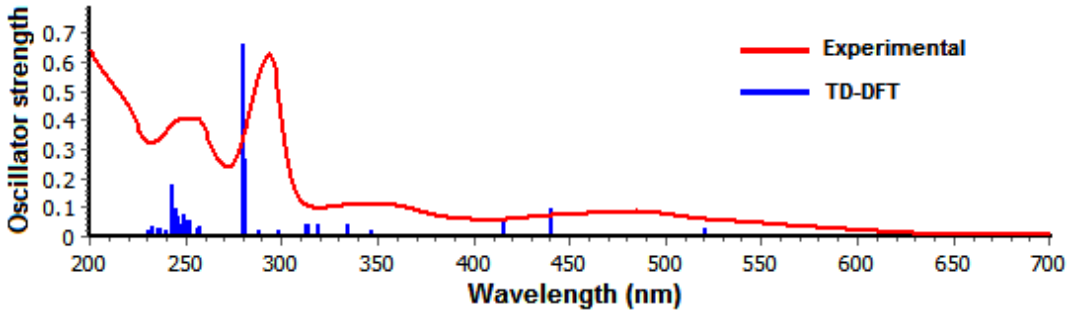


Figure S8: Overlap of experimental electronic absorption spectrum with oscillator strength from TD-DFT calculation of $\mathbf{2}^{2+}$ in (*S=0*) ground state with first seventy calculated transitions.

Table S4. Selected Transitions from TD-DFT calculations of $\mathbf{2}^{2+}$ in the Singlet Ground State (b3lyp/LanL2DZ(f)[Ru]6−31G**[C,H,N,O], CPCM (CH_3CN)).

energy (eV)	λ/nm	λ/nm (ε x 10^3 $M^{-1}cm^{-1}$) [expt.]	f	Major transition(s)	character
5.13	242	246 (33.1)	0.1757	H-6->L+2 (37%), H-4->L+5 (10%)	Bpy/Pyrimidine/hpp(n/π) to Bpy/Pyrimidine/hpp(π∗)
5.08	244	255 (33.5)	0.0928	H-4->L+3 (64%)	Pyrimidine/hpp(n/π) to Bpy/Pyrimidine/hpp(π∗)
4.45	278	293 (51.6)	0.658	H-6->L (28%), H-5->L+1 (37%)	Bpy(π) to Bpy (π∗)
3.72	333	353 (9.4)	0.0406	H-2->L+2 (82%)	Ru(dπ) to Bpy(π*)
2.82	439	493 (6.9)	0.0953	H-2->L (42%), H-1->L (27%), H-1->L+1 (24%)	Ru(dπ) to Bpy(π*)
2.39	519	542 (3.9)	0.0259	H->L (33%), H->L+1 (56%)	Ru(dπ) to Bpy(π*) (major) + hpp(n/π) to Bpy(π*) (minor)

Table S5. MO Composition of $\mathbf{3}^{2+}$ in Singlet (*S*=0) Ground State (b3lyp/LanL2DZ(f)[Ru]6−31G**[C,H,N,O]).

MO	Energy (eV)	Composition				
		Ru	BPy	Pyrimidine	Hpp	Adduct (Butoxy)
LUMO+6	-1.24	2	64	28	3	3
LUMO+5	-1.35	2	53	37	5	3
LUMO+4	-1.38	3	76	19	1	2
LUMO+3	-1.48	2	50	45	3	0
LUMO+2	-1.62	2	83	14	1	0
LUMO+1	-2.38	6	93	1	0	0
LUMO	**-2.45**	**3**	**97**	**0**	**0**	**0**
HOMO	**-5.56**	**63**	**10**	**1**	**26**	**0**
HOMO-1	-6.01	79	13	6	1	2
HOMO-2	-6.08	80	16	1	3	0
HOMO-3	-7.03	18	8	10	60	4
HOMO-4	-7.13	1	12	27	55	6
HOMO-5	-7.25	1	96	2	1	1
HOMO-6	-7.29	1	89	2	7	1

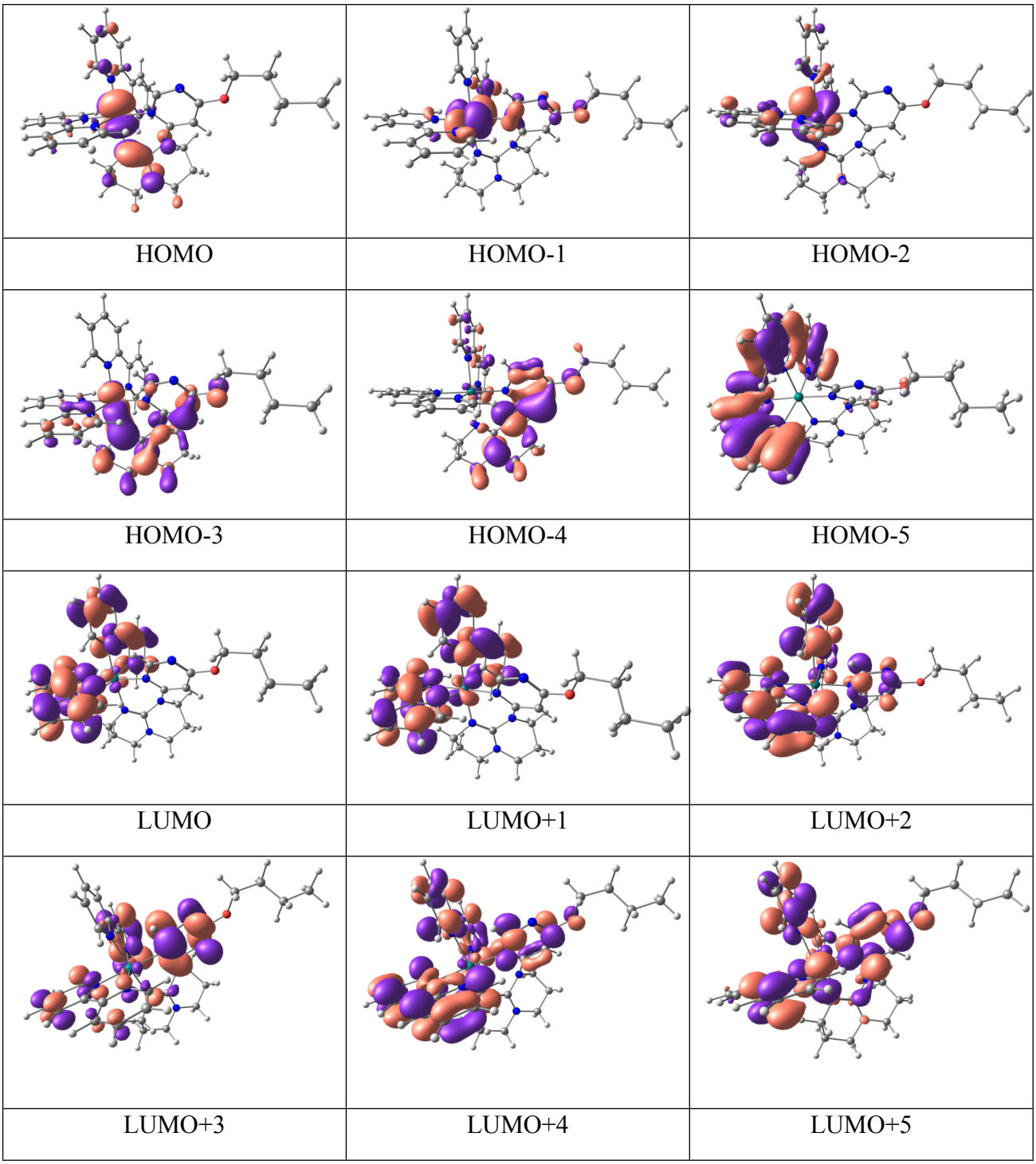


Figure S9. Kohn-Sham molecular orbital sketches for $\mathbf{3}^{2+}$ in (*S=0*) ground state

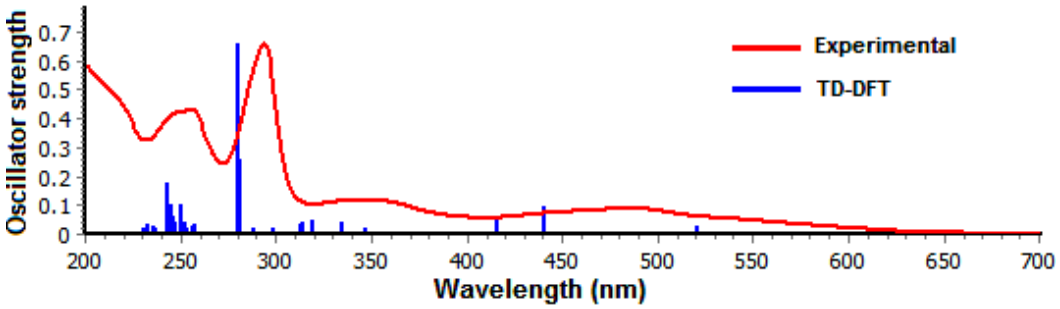


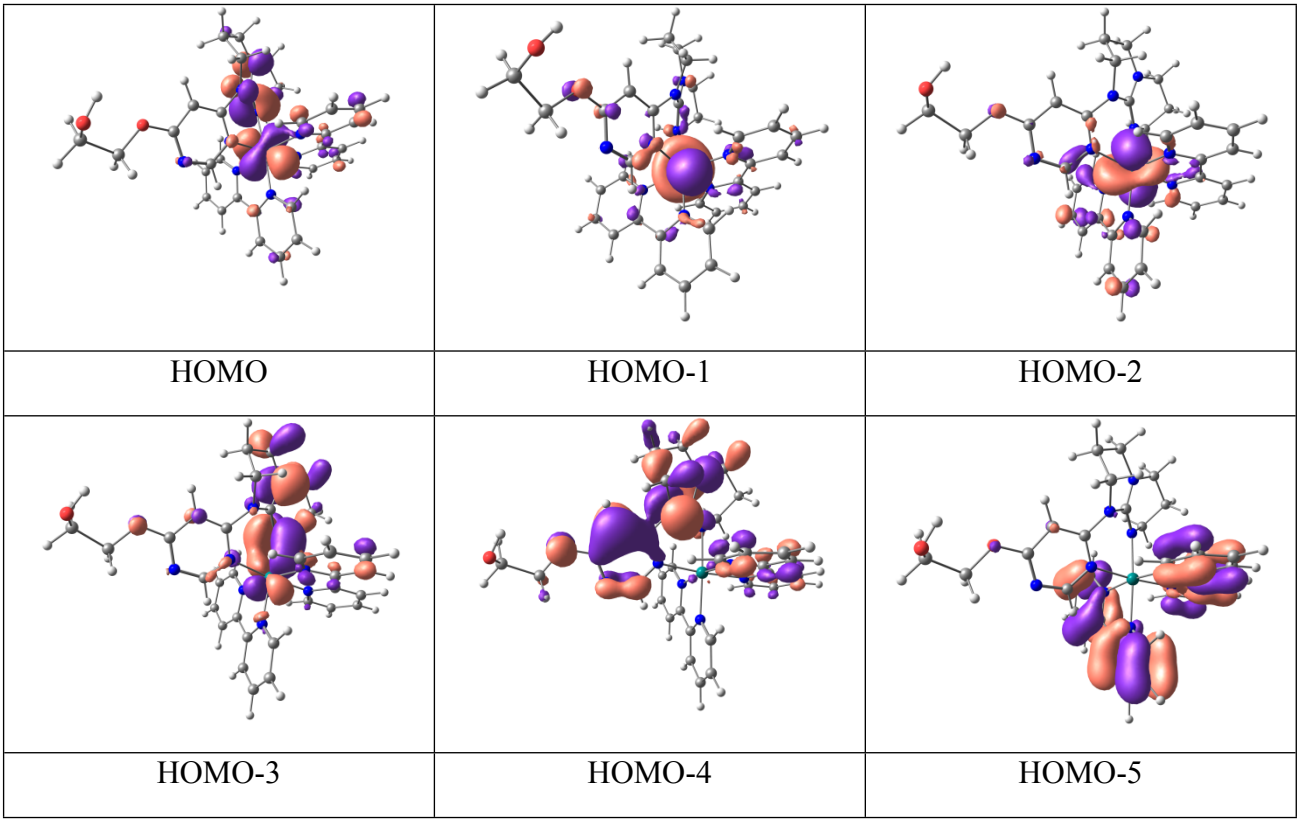
Figure S10. Overlap of experimental electronic absorption spectrum with oscillator strength from TD-DFT calculation of $\mathbf{3}^{2+}$ in (*S=0*) ground state with first seventy calculated transitions.

Table S6. Selected Transitions from TD-DFT calculations of $\mathbf{3}^{2+}$ in the Singlet Ground State (b3lyp/LanL2DZ(f)[Ru]6−31G**[C,H,N,O], CPCM (CH_3CN)).

energy (eV)	λ/nm	λ/nm (ε x 10^3 $M^{-1}cm^{-1}$) [expt.]	f	Major transition(s)	character
5.13	242	248 (25.2)	0.1761	H-6->L+2 (30%), H-4->L+5 (12%)	Bpy/Pyrimidine/hpp(n/π) to Bpy/Pyrimidine/hpp(π*)
4.98	249	255 (25.7)	0.1048	H-7->L (38%), H-4->L+5 (10%), H->L+12 (11%)	Pyrimidine/hpp(n/π) to Bpy/Pyrimidine/hpp(π*)
4.45	279	294 (39.1)	0.6574	H-6->L (28%), H-5->L+1 (38%)	Bpy(π) to Bpy (π*)
3.72	334	354 (6.9)	0.0406	H-2->L+2 (82%)	Ru(dπ) to Bpy(π*)
2.82	440	494 (5.3)	0.0939	H-2->L (43%), H-1->L (27%), H-1->L+1 (23%)	Ru(dπ) to Bpy(π*)
2.38	520	552 (2.8)	0.0254	H->L (32%), H->L+1 (57%)	Ru(dπ) to Bpy(π*) (major) + hpp(n/π) to Bpy(π*) (minor)

Table S7. MO Composition of $\mathbf{4}^{2+}$ in Singlet (*S*=0) Ground State (b3lyp/LanL2DZ(f)[Ru]6−31G**[C,H,N,O]).

MO	Energy (eV)	Composition				
		Ru	BPy	Pyrimidine	Hpp	Adduct (ethylene glycol)
LUMO+6	-1.3	2	83	13	1	1
LUMO+5	-1.38	4	61	30	1	3
LUMO+4	-1.39	1	68	24	4	2
LUMO+3	-1.48	1	17	75	7	0
LUMO+2	-1.62	2	87	10	0	1
LUMO+1	-2.38	6	92	1	1	0
LUMO	**-2.47**	**3**	**97**	**0**	**0**	**0**
HOMO	**-5.65**	**59**	**12**	**2**	**27**	**0**
HOMO-1	-5.90	82	10	4	3	1
HOMO-2	-6.14	81	15	3	1	1
HOMO-3	-7.04	18	9	3	69	1
HOMO-4	-7.16	1	11	29	53	6
HOMO-5	-7.26	0	97	1	1	0



HOMO | HOMO-1 | HOMO-2

HOMO-3 | HOMO-4 | HOMO-5

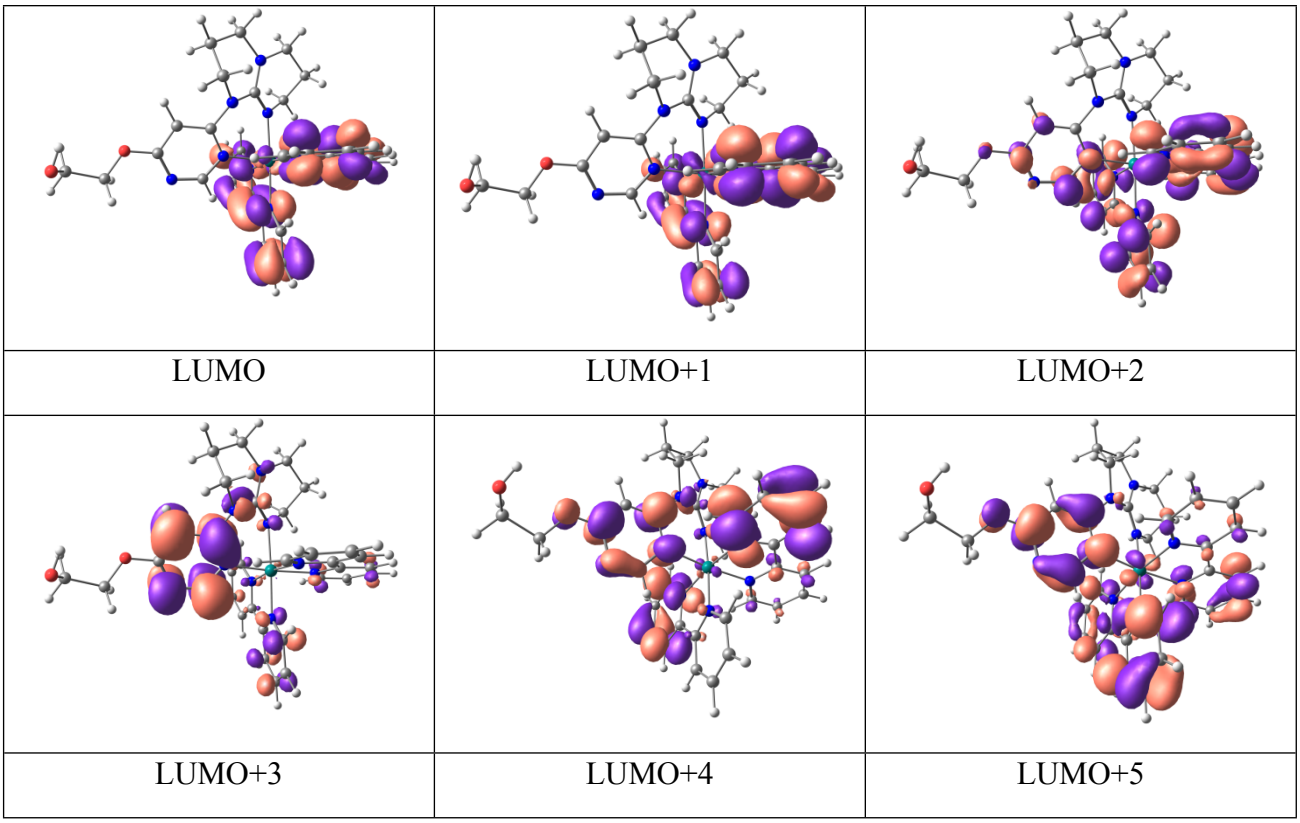


Figure S11. Kohn-Sham Electron density sketches for $\mathbf{4}^{2+}$ in (*S=0*) ground state

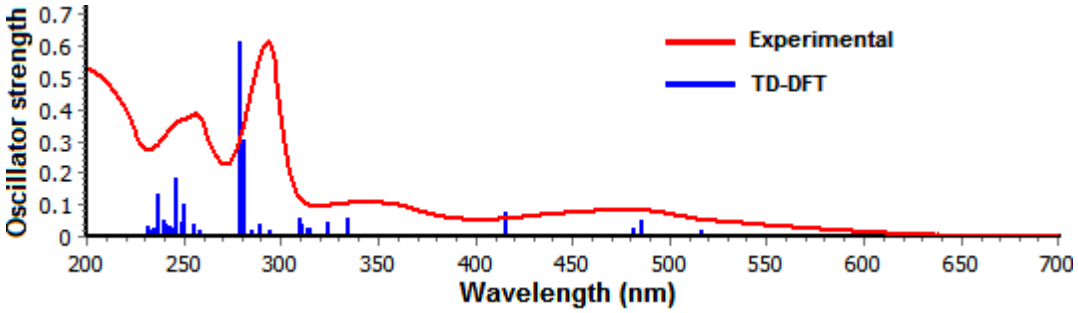


Figure S12. Overlap of experimental electronic absorption spectra with oscillator strength from TD-DFT calculation of $\mathbf{4}^{2+}$ in (*S=0*) ground state with first seventy calculated transitions.

Table S8. Selected Transitions from TD-DFT calculations of $\mathbf{4}^{2+}$ in the Singlet Ground State (b3lyp/LanL2DZ(f)[Ru]6−31G**[C,H,N,O], CPCM (CH_3CN)).

energy (eV)	λ/nm	λ/nm (ε x 10^3 $M^{-1}cm^{-1}$) [expt.]	f	Major transition(s)	character
5.06	245	248 (15.2)	0.1819	H-4->L+2 (21%), H-4->L+3 (12%), H-3->L+5 (15%)	Bpy/Pyrimidine/hpp(n/π) to Bpy/Pyrimidine/hpp(π∗)
4.98	249	256 (15.9)	0.1039	H-4->L+3 (19%), H-3->L+4 (28%)	Pyrimidine/hpp(n/π) to Bpy/Pyrimidine/hpp(π∗)
4.45	278	293 (25.4)	06113	H-6->L (18%), H-5->L+1 (38%)	Bpy(π) to Bpy (π∗)
3.72	333	346 (4.5)	0.0589	H-1->L+4 (59%), H-1->L+5 (24%)	Ru(dπ) to Bpy(π*) + Ru(dπ) to Pyrm(π*)
2.56	484	483 (3.5)	0.0486	H-1->L+1 (44%), H->L+1 (39%)	Ru(dπ) to Bpy(π*) (major) + hpp(n/π) to Bpy(π*) (minor)
2.40	515	538 (1.6)	0.0208	H->L (80%), H->L+1 (15%)	Ru(dπ) to Bpy(π*) (major) + hpp(n/π) to Bpy(π*) (minor)

Table **S9**. Optimized Atomic coordinates obtained from DFT for **1**(***meso***)$^{2+}$ 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	3.062815	-0.294443	-0.175592
2	44	0	-3.062849	-0.294442	0.175534
3	7	0	1.208079	0.821462	-0.008900
4	7	0	-1.208136	0.821497	0.008645
5	7	0	3.915198	0.286553	1.674917
6	7	0	4.971169	-1.179067	-0.265964
7	7	0	2.403549	-2.193621	0.485164
8	7	0	2.347910	-1.165087	-1.958012
9	7	0	2.408895	2.890531	0.204154
10	7	0	4.295256	3.791470	-0.882977
11	7	0	3.791440	1.494823	-1.094408
12	7	0	-3.915447	0.286585	-1.674857
13	7	0	-4.971121	-1.179297	0.266003
14	7	0	-2.347894	-1.165033	1.957975
15	7	0	-2.403431	-2.193518	-0.485242
16	7	0	-2.408898	2.890651	-0.204082
17	7	0	-4.295359	3.791421	0.883026
18	7	0	-3.791368	1.494829	1.094418
19	6	0	-0.000045	0.230738	-0.000177
20	1	0	-0.000060	-0.850880	-0.000258
21	6	0	-1.214876	2.187948	-0.037896
22	6	0	0.000000	2.877512	0.000010
23	1	0	0.000028	3.956027	0.000144
24	6	0	1.214853	2.187907	0.037793
25	6	0	3.294753	0.962661	2.663209
26	1	0	2.260813	1.225420	2.476820
27	6	0	3.916191	1.306938	3.857932
28	1	0	3.365954	1.848614	4.619502
29	6	0	5.249199	0.940254	4.048872
30	1	0	5.773406	1.195802	4.963949
31	6	0	5.893720	0.224360	3.045393
32	1	0	6.922106	-0.084026	3.186087
33	6	0	5.207945	-0.102456	1.868898
34	6	0	5.796716	-0.914541	0.786823
35	6	0	7.101228	-1.419237	0.825213
36	1	0	7.751636	-1.199598	1.662595
37	6	0	7.570397	-2.214262	-0.217057
38	1	0	8.580946	-2.608860	-0.194372
39	6	0	6.715671	-2.492458	-1.282632
40	1	0	7.032394	-3.108925	-2.116703
41	6	0	5.432299	-1.956565	-1.266847
42	1	0	4.747411	-2.141291	-2.084912
43	6	0	2.465887	-2.650433	1.751523
44	1	0	2.681243	-1.909600	2.512205
45	6	0	2.301244	-3.991967	2.080583

46	1	0	2.388586	-4.308247	3.114367
47	6	0	2.063326	-4.909237	1.056516
48	1	0	1.966690	-5.969062	1.269615
49	6	0	1.968833	-4.443020	-0.252237
50	1	0	1.795585	-5.142926	-1.060509
51	6	0	2.134785	-3.079189	-0.518833
52	6	0	2.045957	-2.494031	-1.873342
53	6	0	1.676777	-3.221789	-3.010492
54	1	0	1.454063	-4.279193	-2.936953
55	6	0	1.607179	-2.586667	-4.247998
56	1	0	1.343263	-3.147551	-5.138771
57	6	0	1.884373	-1.220925	-4.319003
58	1	0	1.839643	-0.683289	-5.259847
59	6	0	2.244645	-0.551185	-3.154288
60	1	0	2.480078	0.505705	-3.160144
61	6	0	-3.295231	0.963092	-2.663023
62	1	0	-2.261286	1.225893	-2.476707
63	6	0	-3.916900	1.307713	-3.857524
64	1	0	-3.366843	1.849705	-4.618998
65	6	0	-5.249895	0.940941	-4.048371
66	1	0	-5.774296	1.196777	-4.963257
67	6	0	-5.894168	0.224611	-3.045042
68	1	0	-6.922550	-0.083810	-3.185667
69	6	0	-5.208164	-0.102554	-1.868775
70	6	0	-5.796691	-0.914983	-0.786825
71	6	0	-7.100995	-1.420188	-0.825380
72	1	0	-7.751394	-1.200813	-1.662838
73	6	0	-7.569978	-2.215415	0.216830
74	1	0	-8.580369	-2.610409	0.194010
75	6	0	-6.715285	-2.493276	1.282500
76	1	0	-7.031867	-3.109844	2.116549
77	6	0	-5.432080	-1.956949	1.266831
78	1	0	-4.747226	-2.141465	2.084975
79	6	0	-2.244698	-0.551184	3.154275
80	1	0	-2.480149	0.505702	3.160171
81	6	0	-1.884452	-1.220958	4.318986
82	1	0	-1.839776	-0.683351	5.259849
83	6	0	-1.607193	-2.586681	4.247938
84	1	0	-1.343316	-3.147598	5.138701
85	6	0	-1.676704	-3.221754	3.010400
86	1	0	-1.453934	-4.279145	2.936841
87	6	0	-2.045859	-2.493964	1.873267
88	6	0	-2.134566	-3.079080	0.518727
89	6	0	-1.968368	-4.442867	0.252073
90	1	0	-1.795082	-5.142792	1.060318
91	6	0	-2.062679	-4.909034	-1.056716
92	1	0	-1.965837	-5.968833	-1.269850
93	6	0	-2.300692	-3.991754	-2.080752
94	1	0	-2.387919	-4.307980	-3.114562
95	6	0	-2.465621	-2.650269	-1.751626
96	1	0	-2.681141	-1.909444	-2.512270
97	6	0	2.386939	4.159620	0.972940

98	1	0	1.470437	4.195436	1.560429
99	1	0	3.220941	4.124547	1.682765
100	6	0	2.546920	5.336901	0.021538
101	1	0	1.744878	5.332349	-0.725072
102	1	0	2.494108	6.289765	0.555006
103	6	0	3.911846	5.199441	-0.641849
104	1	0	3.951269	5.735833	-1.596400
105	1	0	4.683376	5.635197	0.003574
106	6	0	5.648847	3.678949	-1.479299
107	1	0	6.345320	4.222642	-0.831641
108	1	0	5.628191	4.198906	-2.444063
109	6	0	6.072518	2.229273	-1.660373
110	1	0	6.882158	2.176079	-2.393196
111	1	0	6.448271	1.810339	-0.721133
112	6	0	4.850756	1.439776	-2.120871
113	1	0	5.094325	0.397233	-2.311442
114	1	0	4.475497	1.865855	-3.062440
115	6	0	3.539212	2.694252	-0.626249
116	6	0	-2.387011	4.159830	-0.972728
117	1	0	-3.221045	4.124824	-1.682511
118	1	0	-1.470544	4.195775	-1.560260
119	6	0	-2.546976	5.336986	-0.021166
120	1	0	-1.744901	5.332339	0.725407
121	1	0	-2.494181	6.289910	-0.554523
122	6	0	-3.911884	5.199428	0.642269
123	1	0	-3.951220	5.735582	1.596965
124	1	0	-4.683419	5.635415	-0.002999
125	6	0	-5.649113	3.678764	1.478940
126	1	0	-6.345503	4.222093	0.830880
127	1	0	-5.628889	4.199021	2.443551
128	6	0	-6.072549	2.229034	1.660294
129	1	0	-6.448277	1.809888	0.721143
130	1	0	-6.882157	2.175818	2.393155
131	6	0	-4.850670	1.439788	2.120907
132	1	0	-4.475448	1.866100	3.062380
133	1	0	-5.094095	0.397242	2.311662
134	6	0	-3.539226	2.694274	0.626257

Table **S10**. Optimized Atomic coordinates obtained from DFT for $\mathbf{2}^{2+}$ in singlet ground state (b3lyp/LanL2DZ(f)[Ru]6−31G**[C,H,N,O]).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	0.733662	-0.117171	0.010315
2	8	0	-5.288412	-1.226899	-0.873688
3	7	0	0.989790	-2.156665	0.468786
4	7	0	0.361377	-0.162320	2.088702
5	7	0	2.820372	0.089615	0.155925
6	7	0	1.331538	-0.239909	-2.008362
7	7	0	-1.359282	-0.373592	-0.334468
8	7	0	-3.077730	-1.886520	-1.042343
9	7	0	-1.887763	1.781727	0.553154
10	7	0	-1.020024	3.891014	-0.010482
11	7	0	0.305227	1.953773	-0.314201
12	6	0	1.392720	-3.113880	-0.391797
13	1	0	1.639421	-2.779801	-1.392608
14	6	0	1.481240	-4.456688	-0.044051
15	1	0	1.809277	-5.183112	-0.779156
16	6	0	1.134387	-4.836976	1.252213
17	1	0	1.180267	-5.876504	1.559022
18	6	0	0.732885	-3.855103	2.152314
19	1	0	0.469717	-4.131637	3.165630
20	6	0	0.676450	-2.517163	1.745860
21	6	0	0.334002	-1.403797	2.651516
22	6	0	0.058374	-1.572569	4.013610
23	1	0	0.028541	-2.563732	4.448580
24	6	0	-0.162727	-0.459890	4.818263
25	1	0	-0.373159	-0.581367	5.875619
26	6	0	-0.089863	0.809123	4.243070
27	1	0	-0.230437	1.706781	4.834987
28	6	0	0.169656	0.910610	2.881370
29	1	0	0.237181	1.872535	2.389308
30	6	0	0.512507	-0.313395	-3.076089
31	1	0	-0.548603	-0.286721	-2.862824
32	6	0	0.977658	-0.417366	-4.382267
33	1	0	0.270629	-0.476941	-5.202170
34	6	0	2.354221	-0.440228	-4.603974
35	1	0	2.755880	-0.522633	-5.608400
36	6	0	3.209482	-0.343990	-3.510221
37	1	0	4.281236	-0.342489	-3.665251
38	6	0	2.680519	-0.238777	-2.219138
39	6	0	3.511101	-0.085106	-1.007731
40	6	0	4.910107	-0.084527	-1.023114
41	1	0	5.448684	-0.234202	-1.950610
42	6	0	5.615371	0.108376	0.160903
43	1	0	6.700234	0.109849	0.158554
44	6	0	4.901384	0.300216	1.343210
45	1	0	5.405594	0.458976	2.289905

46	6	0	3.512040	0.279873	1.296223
47	1	0	2.920737	0.415821	2.193205
48	6	0	-2.300840	0.562168	-0.009979
49	6	0	-3.650257	0.285706	-0.198864
50	1	0	-4.433656	1.000872	0.003295
51	6	0	-4.005807	-0.974916	-0.710009
52	6	0	-1.820792	-1.533406	-0.846940
53	1	0	-1.064223	-2.260438	-1.118941
54	6	0	-2.866528	2.546042	1.354452
55	1	0	-2.332442	2.975023	2.209427
56	1	0	-3.605196	1.853846	1.754488
57	6	0	-3.468404	3.649384	0.494773
58	1	0	-4.226373	4.217100	1.041344
59	1	0	-3.955780	3.213581	-0.382733
60	6	0	-2.326529	4.576607	0.084092
61	1	0	-2.534130	5.068582	-0.873823
62	1	0	-2.206219	5.369924	0.831206
63	6	0	0.082405	4.835778	-0.274565
64	1	0	0.028818	5.633634	0.475046
65	1	0	-0.092701	5.300439	-1.253321
66	6	0	1.434305	4.142568	-0.248846
67	1	0	2.183644	4.782553	-0.722909
68	1	0	1.760742	3.962672	0.781564
69	6	0	1.301473	2.811216	-0.979608
70	1	0	1.008697	2.980613	-2.025260
71	1	0	2.252443	2.283861	-0.990596
72	6	0	-0.816590	2.541071	0.033107
73	6	0	-5.702454	-2.516273	-1.434098
74	1	0	-5.327335	-3.306839	-0.778843
75	1	0	-5.229256	-2.628716	-2.413220
76	6	0	-7.213677	-2.498876	-1.517462
77	1	0	-7.662444	-2.373619	-0.528747
78	1	0	-7.561034	-3.449038	-1.933133
79	1	0	-7.564019	-1.692894	-2.167324

Table **S11**. Optimized Atomic coordinates obtained from DFT for $\mathbf{3}^{2+}$ in singlet ground state (b3lyp/LanL2DZ(f)[Ru]6−31G**[C,H,N,O]).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	-1.108242	-0.157866	-0.022975
2	8	0	5.050487	-0.700974	0.042926
3	7	0	1.024975	-0.219568	-0.044933
4	7	0	2.958915	-1.594508	-0.377584
5	7	0	-1.382810	-0.477810	-2.089406
6	7	0	-3.203983	-0.162249	-0.193769
7	7	0	-1.242735	-2.177792	0.560473
8	7	0	-1.050144	-0.023627	2.084739
9	7	0	1.215435	2.034330	0.726553
10	7	0	0.246998	3.999094	-0.123260
11	7	0	-0.829168	1.918042	-0.455835
12	6	0	1.660354	-1.358795	-0.389833
13	1	0	1.019276	-2.174995	-0.703237
14	6	0	3.741219	-0.571609	0.004171
15	6	0	3.199905	0.678289	0.355662
16	1	0	3.876814	1.481506	0.606032
17	6	0	1.818110	0.827750	0.330302
18	6	0	-0.409537	-0.528195	-3.019908
19	1	0	0.598277	-0.365439	-2.659325
20	6	0	-0.660520	-0.771304	-4.365682
21	1	0	0.163467	-0.804685	-5.069646
22	6	0	-1.978790	-0.965697	-4.777049
23	1	0	-2.214807	-1.160813	-5.817826
24	6	0	-2.994046	-0.893311	-3.827672
25	1	0	-4.024885	-1.023434	-4.132907
26	6	0	-2.678256	-0.642331	-2.487905
27	6	0	-3.691845	-0.497166	-1.423355
28	6	0	-5.065966	-0.651837	-1.635764
29	1	0	-5.442605	-0.928912	-2.612577
30	6	0	-5.955891	-0.448783	-0.585295
31	1	0	-7.023051	-0.566876	-0.740748
32	6	0	-5.449645	-0.089433	0.663292
33	1	0	-6.103371	0.085700	1.510408
34	6	0	-4.073581	0.038808	0.815037
35	1	0	-3.638157	0.308233	1.769241
36	6	0	-1.418268	-3.227901	-0.267452
37	1	0	-1.538043	-2.989638	-1.317490
38	6	0	-1.434685	-4.546026	0.173169
39	1	0	-1.576903	-5.350666	-0.539564
40	6	0	-1.258537	-4.799493	1.533286
41	1	0	-1.255329	-5.814922	1.915057
42	6	0	-1.092880	-3.722450	2.398115
43	1	0	-0.964916	-3.901037	3.458420
44	6	0	-1.097735	-2.416565	1.894945
45	6	0	-1.000580	-1.215025	2.745882

46	6	0	-0.924161	-1.262918	4.142907
47	1	0	-0.874905	-2.214488	4.657257
48	6	0	-0.927411	-0.082126	4.877734
49	1	0	-0.873047	-0.110295	5.960907
50	6	0	-1.018837	1.131446	4.195651
51	1	0	-1.048019	2.076947	4.725862
52	6	0	-1.074002	1.114081	2.806961
53	1	0	-1.145974	2.030059	2.234800
54	6	0	1.989996	2.948183	1.592163
55	1	0	2.723755	2.364742	2.145295
56	1	0	1.298898	3.374365	2.328049
57	6	0	2.604883	4.048727	0.737790
58	1	0	3.250863	3.607574	-0.027415
59	1	0	3.220713	4.726255	1.335500
60	6	0	1.452609	4.823963	0.103383
61	1	0	1.750647	5.278275	-0.849269
62	1	0	1.148265	5.642536	0.766272
63	6	0	-0.889157	4.803617	-0.612886
64	1	0	-0.614390	5.224272	-1.588625
65	1	0	-1.025842	5.646578	0.074234
66	6	0	-2.157065	3.974290	-0.729775
67	1	0	-2.882923	4.500392	-1.356001
68	1	0	-2.618050	3.825154	0.253051
69	6	0	-1.787479	2.620704	-1.326588
70	1	0	-2.670469	1.995737	-1.436822
71	1	0	-1.353555	2.753636	-2.327539
72	6	0	0.167715	2.641174	-0.000100
73	6	0	5.663311	-1.977726	-0.341594
74	1	0	5.296271	-2.744737	0.345727
75	1	0	5.323230	-2.225620	-1.351360
76	6	0	7.169204	-1.804079	-0.265588
77	1	0	7.608958	-2.796515	-0.428846
78	1	0	7.444494	-1.510132	0.754857
79	6	0	7.743688	-0.807413	-1.281757
80	1	0	7.280388	0.174707	-1.126687
81	1	0	7.462894	-1.126328	-2.294844
82	6	0	9.266981	-0.680897	-1.185505
83	1	0	9.574976	-0.333349	-0.193420
84	1	0	9.650636	0.031741	-1.921157
85	1	0	9.758142	-1.642737	-1.367494

Table **S12**. Optimized Atomic coordinates obtained from DFT for $\mathbf{4}^{2+}$ in singlet ground state (b3lyp/LanL2DZ(f)[Ru]6−31G**[C,H,N,O]).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	0.797102	-0.293863	-0.021913
2	8	0	-5.395153	-0.343404	0.101943
3	8	0	-7.842996	-0.616654	1.603912
4	1	0	-7.605172	0.310298	1.479784
5	7	0	-1.337007	-0.207269	0.066891
6	7	0	-3.373793	-1.459714	0.205003
7	7	0	1.205926	0.895715	1.667011
8	7	0	2.894848	-0.189865	-0.052006
9	7	0	1.007168	-2.146964	0.966344
10	7	0	0.579598	-1.674098	-1.602837
11	7	0	-1.361293	2.180883	-0.090587
12	7	0	-0.187220	3.682607	-1.464407
13	7	0	0.578581	1.462542	-1.226731
14	6	0	-2.059252	-1.341930	0.171761
15	1	0	-1.487425	-2.257874	0.254642
16	6	0	-4.075751	-0.322976	0.093024
17	6	0	-3.439611	0.922810	-0.052354
18	1	0	-4.043494	1.809302	-0.182487
19	6	0	-2.050168	0.952980	-0.048118
20	6	0	0.298970	1.337374	2.561770
21	1	0	-0.726328	1.044672	2.375451
22	6	0	0.637111	2.111185	3.665898
23	1	0	-0.134980	2.432164	4.356381
24	6	0	1.975811	2.453495	3.859897
25	1	0	2.279180	3.060769	4.706195
26	6	0	2.922455	1.986288	2.954168
27	1	0	3.968581	2.224718	3.100381
28	6	0	2.520275	1.199018	1.868659
29	6	0	3.462163	0.597787	0.905504
30	6	0	4.849212	0.773054	0.966235
31	1	0	5.289190	1.406677	1.726281
32	6	0	5.671019	0.124997	0.049370
33	1	0	6.747341	0.254508	0.090477
34	6	0	5.084404	-0.694970	-0.914122
35	1	0	5.682259	-1.226850	-1.645798
36	6	0	3.700086	-0.821968	-0.929415
37	1	0	3.204462	-1.440321	-1.667997
38	6	0	1.175734	-2.317206	2.292098
39	1	0	1.107743	-1.422025	2.898020
40	6	0	1.426173	-3.557128	2.869151
41	1	0	1.551136	-3.635646	3.943317
42	6	0	1.514900	-4.676192	2.042049
43	1	0	1.717098	-5.659001	2.454510
44	6	0	1.333209	-4.512768	0.671992
45	1	0	1.393100	-5.372344	0.015926

46	6	0	1.072437	-3.240385	0.151969
47	6	0	0.801696	-2.981082	-1.276842
48	6	0	0.721887	-3.988391	-2.244880
49	1	0	0.902314	-5.022028	-1.977069
50	6	0	0.394003	-3.662550	-3.557620
51	1	0	0.330471	-4.437276	-4.314452
52	6	0	0.133080	-2.329506	-3.873880
53	1	0	-0.145308	-2.030071	-4.878120
54	6	0	0.233387	-1.372866	-2.869992
55	1	0	0.030874	-0.327455	-3.062840
56	6	0	-2.039009	3.385050	0.436783
57	1	0	-1.315107	3.932169	1.051783
58	1	0	-2.846538	3.068234	1.094214
59	6	0	-2.510789	4.248942	-0.724894
60	1	0	-3.059075	5.127798	-0.374866
61	1	0	-3.185822	3.674086	-1.366971
62	6	0	-1.266764	4.690803	-1.488432
63	1	0	-1.498961	4.928396	-2.533466
64	1	0	-0.858582	5.602141	-1.034928
65	6	0	1.051929	4.176435	-2.099224
66	1	0	0.818870	4.422890	-3.142515
67	1	0	1.337156	5.111463	-1.602742
68	6	0	2.172383	3.148954	-2.034594
69	1	0	2.655616	3.157620	-1.051911
70	1	0	2.933754	3.390093	-2.781716
71	6	0	1.555240	1.775964	-2.283236
72	1	0	2.311446	0.993671	-2.297934
73	1	0	1.062414	1.772583	-3.266706
74	6	0	-0.281676	2.419748	-0.959678
75	6	0	-6.088254	-1.624731	0.255786
76	1	0	-5.701600	-2.123021	1.146904
77	1	0	-5.882129	-2.240509	-0.624882
78	6	0	-7.565923	-1.309111	0.404912
79	1	0	-7.925652	-0.771194	-0.483927
80	1	0	-8.103978	-2.261817	0.451169

References:

1. G. A. Crosby, J. N. Demas, *J. Phys. Chem.*, 1971, **75**, 991.
2. V. C. Jonathan, J. M. Thomas, *J. Am. Chem. Soc.* 1983, **105**, 5783.
3. G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, D. G. Whitten, *J. Am. Chem. Soc.* 1977, **99**, 4947.
4. A. K. Pal, P. D. Ducharme, G. S. Hanan, *Chem. Commun.*, 2013, accepted, DOI:10.1039/C3CC47856D.
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)*