Supporting Information for:

1,4-Benzene-Bridged Covalent Hybrid of Triarylamine and Cyclometalated Ruthenium: A New Type of Organic-Inorganic Mixed-Valent System

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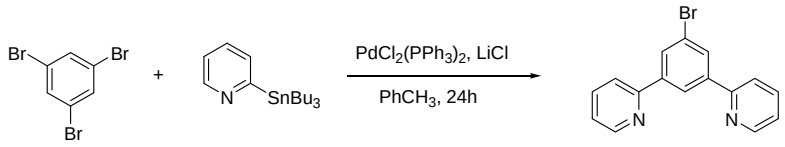
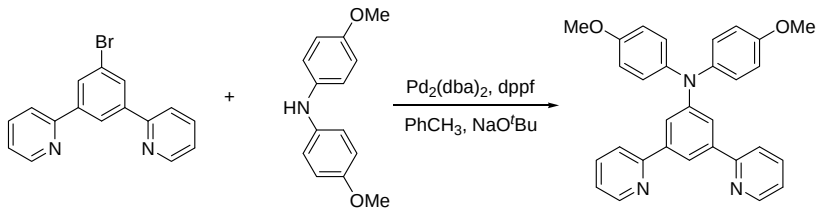
1. Synthetic Procedures and Characterization

General. NMR spectra were recorded in the designated solvent on Bruker Avance 400 MHz spectrometer. Spectra are reported in ppm values from residual protons of deuterated solvent for ^{1}H NMR (δ 7.26 ppm for $CDCl_3$ and 1.92 ppm for CD_3CN) and ^{13}C NMR (δ 77.00 ppm for $CDCl_3$). MS data were obtained with a Bruker Daltonics Inc. ApexII FT-ICR or Autoflex III MALDI-TOF mass spectrometer. The matrix for MALDI-TOF measurement is α-cyano-4-hydroxycinnamic acid. Microanalysis was carried out using Flash EA 1112 or Carlo Erba 1106 analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

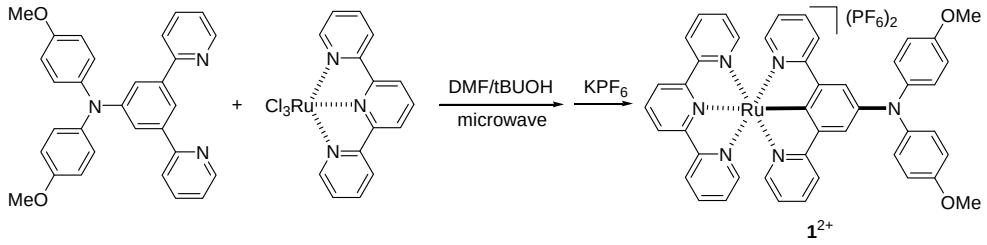


To a solution of 1,3,5-tribromobenzene (1.0 mmol, 320 mg) and 2-(tributylstannyl)pyridine (2.2 mmol, 810 mg) in 20 mL dry toluene were added $PdCl_2(PPh_3)_2$ (0.2 mmol, 140 mg) and LiCl (10 mmol, 424 mg) under a N_2 atmosphere. The mixture was bubbled with nitrogen for 10 min before the vial was capped and heated at 150 ^{0}C for 48 h. After the reaction was cooled to room temperature, the solvent was removed under reduced pressure. The residue was then subjected to column chromatography on silica gel (eluent: CH_2Cl_2/ethyl acetate/NH_4OH 100/10/0.05) to afford 106 mg 3,5-di(2-pyridyl)bromobenzene as a yellow solid in a yield of 34%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (m, 2H), 7.80 (m, 4H), 8.21 (s, 2H), 8.54 (s,1H), 8.70 (d, J = 4.6 Hz, 2 H).



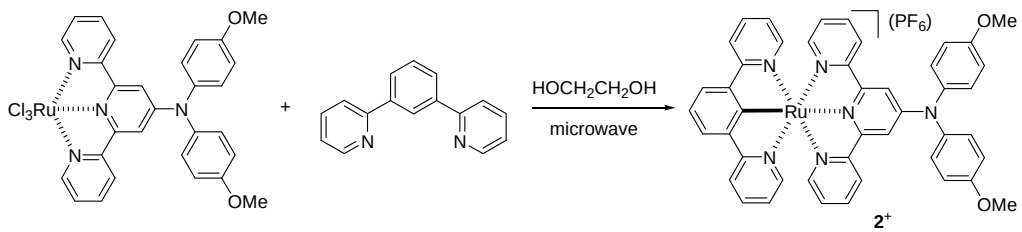
To a solution of 3,5-di(2-pyridyl)bromobenzene (1.0 mmol, 323 mg) and 4,4'-dimethoxydiphenylamine (1.5 mmol, 344 mg) in 20 mL dry toluene were added $Pd_2(dba)_3$ (0.02 mmol, 18.3 mg), 1,1'-bis(diphenylphosphino)ferrocene (dppf) (0.02 mmol, 11.1 mg) and NaO^{t}Bu (1.2 mmol, 115.3 mg) under a N_2 atmosphere. The mixture was bubbled with nitrogen for 10 min before the vial was capped and heated at 130 ^{0}C

for 48 h. After the reaction was cooled to room temperature, the solvent was removed under reduced pressure. The residue was then subjected to column chromatography on silica gel (eluent: CH_2Cl_2/ethyl acetate/NH_4OH 75/6/1) to afford 317 mg 1-di-*p*-anisylamino-3,5-di(2-pyridyl)benzene as a yellow solid in a yield of 69%. ^1H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 6 H), 6.82 (d, J = 8.3Hz, 4 H), 7.10 (d, J = 8.3 Hz, 4 H), 7.18 (t, J = 5.3 Hz, 2 H), 7.65 (s, 2 H), 7.67 (d, J = 5.3 Hz, 4 H), 8.12 (s, 1 H), 8.63 (d, J = 4.3 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 114.7, 118.4, 120.3, 120.8, 122.1, 126.3, 126.4, 136.6, 140.8, 141.1, 149.4, 155.6, 157.2. EI-MS (m/z): 537 $[M + 2K]^+$.



$\mathbf{1}^{2+}$

To a mixture of 3 mL DMF and 3 mL *t*-BuOH were added 1-di-*p*-anisylamino-3,5-di(2-pyridyl)benzene (0.1 mmol, 46 mg) and Ru(tpy)Cl_3 (0.1 mmol, 44 mg). The mixture was heated under microwave conditions for 50 min at a power of 200 W and then another 30 min at a power of 375 W. After cooling down to room temperature, an excess of aqueous KPF_6 were added. The resulting precipitate was collected by filtration and wash successively with water and ether. The crude product was purified by column chromatography on silica using acetonitrile/water/saturated aq. KNO_3 30/1/0.05 as the eluent to give 56 mg [**1**]$(PF_6)_2$ as a black solid (yield: 52%). MALDI-MS (m/z): 792.2 for $[M\text{-}2PF_6]^{2+}$. Anal. Calcd for: $C_{45}H_{35}F_{12}N_6O_2P_2Ru{\cdot}2H_2O$: C, 48.31; H, 3.51; N, 7.51. Found: C, 48.64; H, 3.28; N, 7.65.

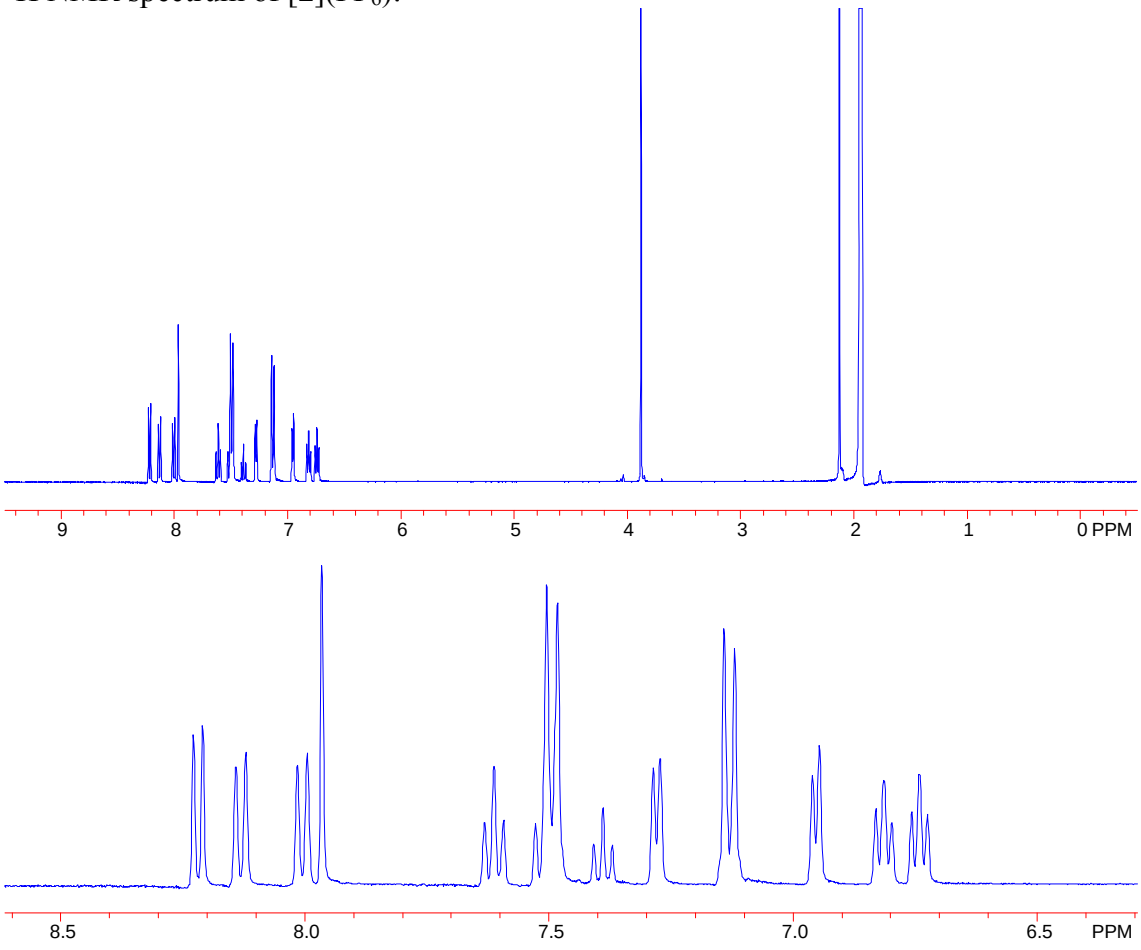


$\mathbf{2}^{+}$

To 5 mL ethylene glycol were added [(2,3-di(2-pyridyl)-4-di-

p-anisylaminopyridine)$RuCl_3$][1] (0.05 mmol, 33.4 mg), 1,3-di(2-pyridyl)benzene (0.05 mmol, 11.6 mg). The mixture was heated under microwave conditions (power = 375 W) for 30 min. After cooling down to room temperature, an excess of aqueous KPF_6 were added. The resulting precipitate was collected by filtration and washing successively with water and ether. The crude product was purified by column chromatography on silica using acetonitrile/water/saturated KNO_3 30/1/0.05 as the eluent to give 16 mg [**2**](PF_6) as a black solid (34% yield). ^{1}H NMR (400 MHz, CD_3CN): δ 3.87 (s, 6 H), 6.74 (t, J = 6.6Hz, 2 H), 6.81 (t, J = 6.6 Hz, 2 H), 6.94 (d, J = 5.5 Hz, 2 H), 7.11 (d, J = 8.6 Hz, 4 H), 7.27 (d, J = 5.5 Hz, 2 H), 7.48-7.52 (m, 6 H), 7.61 (t, J = 7.8 Hz, 2 H), 7.96 (s, 2 H), 7.99 (d, J = 8.0 Hz, 2 H), 8.12 (d, J = 8.0 Hz, 2 H), 8.20 (d, J = 7.5 Hz, 2 H). MALDI-MS (m/z): 793.1 for $[M\text{-}PF_6]^+$. Anal. Calcd. for $C_{45}H_{35}F_6N_6O_2PRu{\cdot}H_2O$: C, 56.54; H, 3.90; N, 8.79. Found: C, 56.05; H, 3.76; N, 8.85.

^{1}H NMR spectrum of [**2**](PF_6):

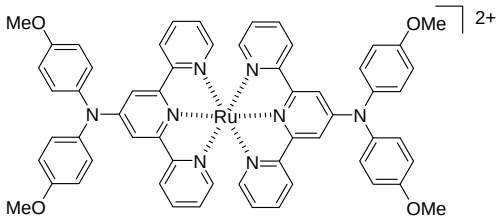


(1) Yao, C.-J.; Yao, J.; Zhong, Y.-W. *Inorg. Chem*. **2011**, *50,* 6847.

2. Computational Method

DFT and TDDFT calculations are carried out using the B3LYP exchange correlation functional[2] and implemented in the *Gaussian* 03 program package.[3] The electronic structures of complexes were determined using a general basis set with the Los Alamos effective core potential LanL2DZ basis set for ruthenium, and 6-31G* for other atoms in vacuum.[4] All orbitals have been computed at an isovalue of 0.02.

The initial structures for $\mathbf{1}^+$ and $\mathbf{2}^+$ were generated on the basis of a known single-crystal structure of the following complex[1] by removing one di-*p*-anisylamino segment and replacing one nitrogen atom with a carbon atom. The calculated lengths of the Ru-C bond for $\mathbf{1}^+$ and $\mathbf{2}^+$ are 1.983 and 1.975 Å, respectively. Other Ru-N lengths are in the range of 2.07~1.15 Å. This is quite reasonable compared to known single-crystal structures of know cyclometalated ruthenium complexes.[5]



(2) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(3) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr. T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision E.01; Gaussian Inc.: Pittsburgh PA, 2007.

(4) (a) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1976; Vol. 3, p 1. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *82*, 270. (c) Wadt, W. R.; Hay, P. J. *J. Chem. Phys*. **1985**, *82*, 284. (d) Hay, P. J.; Wadt, W. R. *J. Chem. Phys*. **1985**, *82*, 299.

(5) (a) Yang, W.-W.; Zhong, Y.-W.; Yoshikawa, S.; Shao, J.-Y.; Masaoka, S.; Sakai, K.; Yao, J.; Haga, M.-a. *Inorg. Chem.* **2012**, *51*, 890. (b) Wadman, S. H.; Havenith, R. W. A.; Hartl, F.; Lutz, M.; Spek, A. L.; van Klink G. P. M.; van Koten, G. *Inorg. Chem.* **2009**, *48*, 5685.

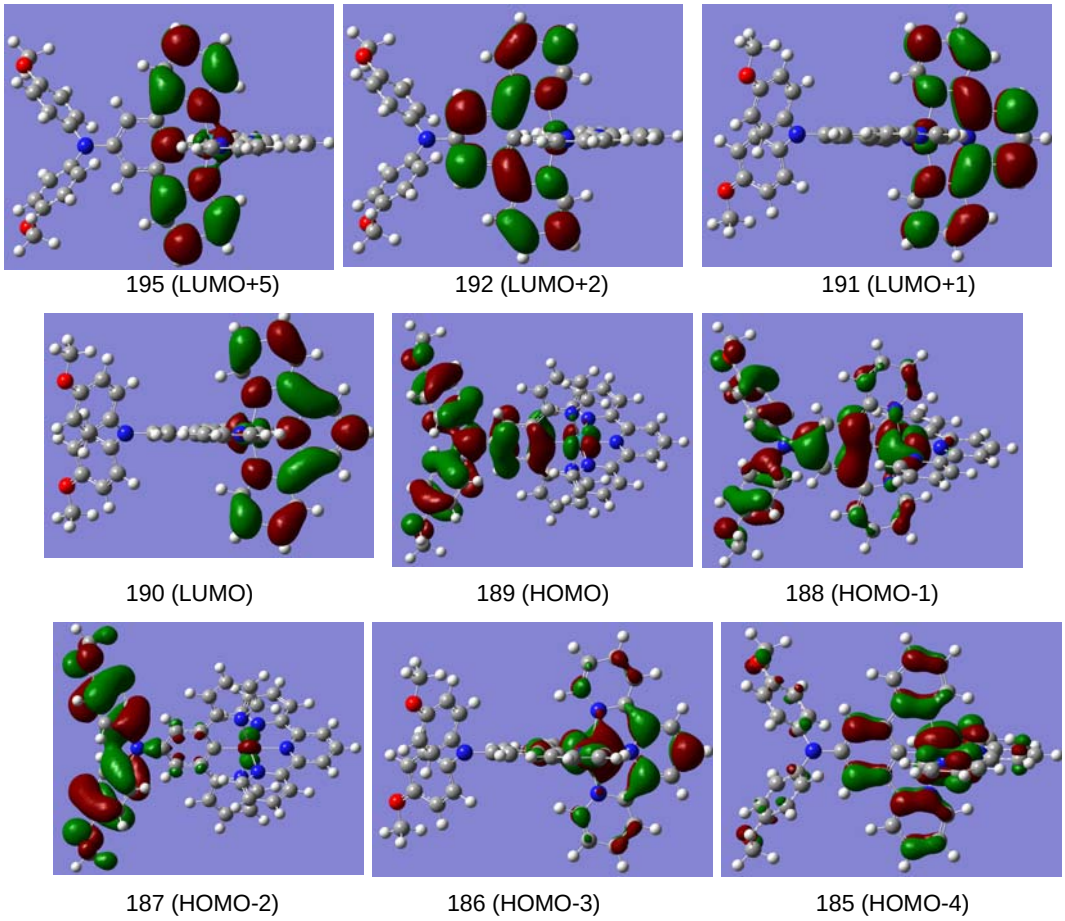


Figure S1. Isodensity plots of selected frontier orbitals for $\mathbf{1}^{+}$.

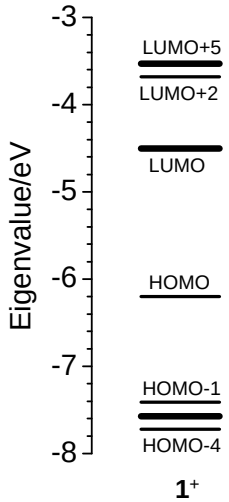


Figure S2. Energy level allignment for $\mathbf{1}^{+}$.

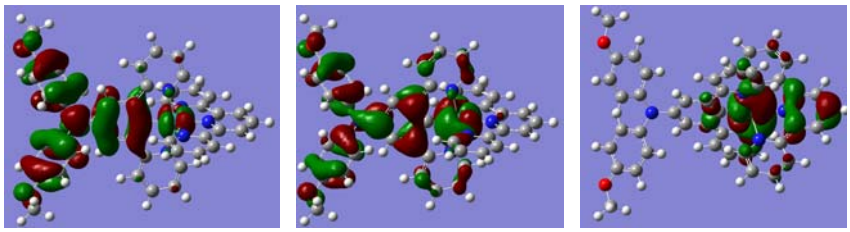


Figure S3. Isodensity plots of selected frontier orbitals for $\mathbf{1}^{2+}$.

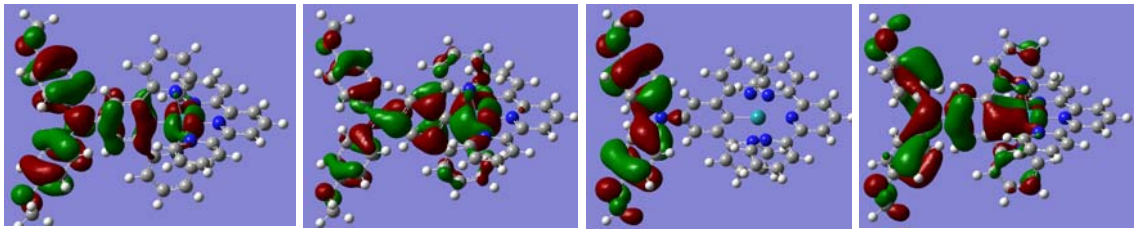


Figure S4. Isodensity plots of selected frontier orbitals for $\mathbf{1}^{3+}$.

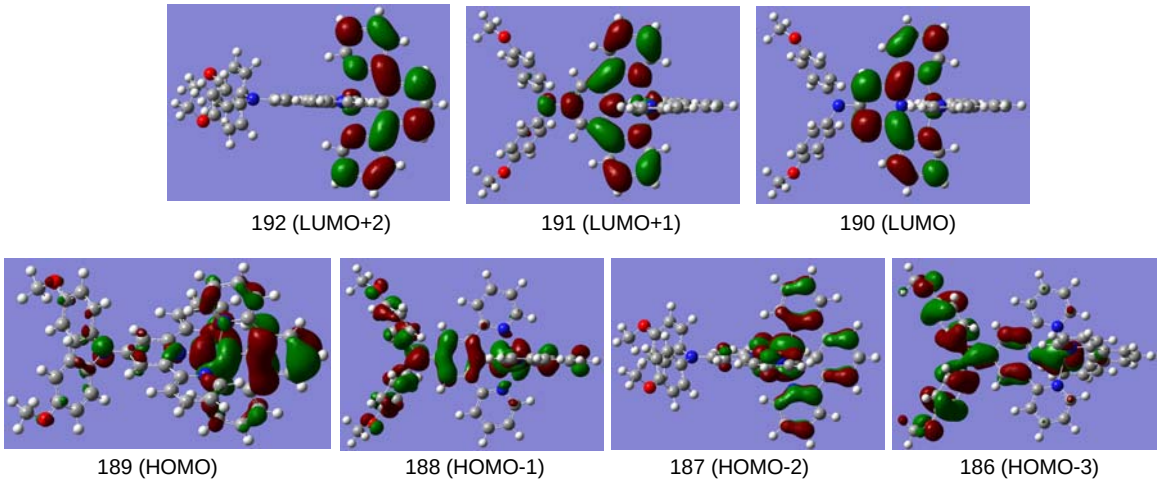


Figure S5. Isodensity plots of selected frontier orbitals for $\mathbf{2}^{+}$.

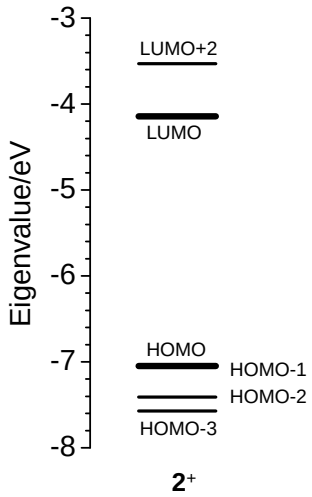


Figure S6. Energy level allignment for $\mathbf{2}^{+}$.

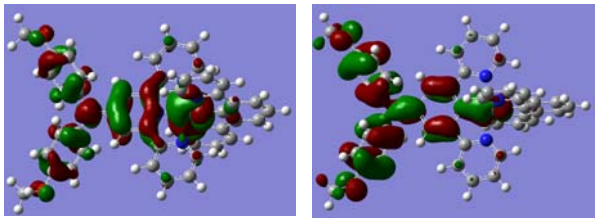


Figure S7. Isodensity plots of selected frontier orbitals for $\mathbf{2}^{2+}$.

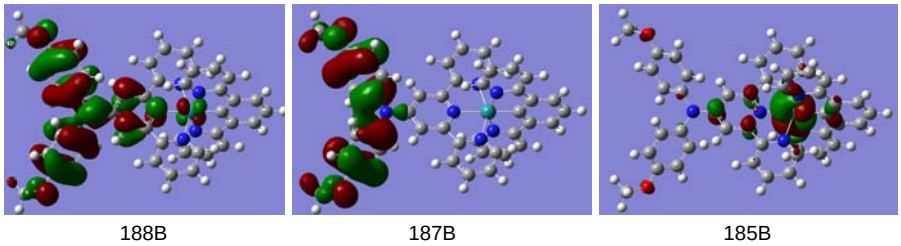


Figure S8. Isodensity plots of selected frontier orbitals for $\mathbf{2}^{3+}$.

Table S1. Calculated main low-energy excitations of complexes studied.[a]

compoumd	S_n	E/eV	E/nm	f	dominant transitions (configuration coefficient)
1^{+}	3	2.01	616	0.0347	189 (HOMO) → 192 (LUMO+2) (0.703)
	6	2.23	556	0.0185	189 (HOMO) → 195 (LUMO+5) (0.68)
	11	2.34	531	0.0437	186 (HOMO-3) → 191 (LUMO+1) (0.657);
					185 (HOMO-4) → 190 (LUMO) (0.209)
	12	2.68	463	0.1215	185 (HOMO-4) →191 (LUMO+1) (0.4192);
					186 (HOMO-3) → 190 (LUMO) (0.4555)
1^{2+}	1	1.20	1036	0.102	187B → 189B (0.81); 188B → 189B (-0.55)
	2	1.23	1007	0.244	187B → 189B (0.58); 188B → 189B (0.75)
1^{3+}	5	1.64	756	0.191	187B → 189B (0.98)
	7	1.74	712	0.1104	182B → 188B (0.8964)
2^{+}	3	2.14	578	0.0154	188 (HOMO-1) → 190 (LUMO) (0.654)
	4	2.27	545	0.0783	188 (HOMO-1) → 191 (LUMO+1) (0.568)
	5	2.40	516	0.0353	187 (HOMO-2) → 191 (LUMO+1) (0.682)
	6	2.61	475	0.1515	187 (HOMO-2) → 190 (LUMO) (0.62)
	7	2.78	445	0.0627	189 (HOMO) → 192 (LUMO+2) (0.67)
2^{2+}	3	0.92	1346	0.290	188B → 189B (0.91)
2^{3+}	3	1.39	892	0.208	187B → 188B (0.9976)
	6	1.55	799	0.134	185B → 188B (0.9677)

[a]Calculated on the level of B3LYP/LanL2DZ/6-31G*/vacuum theory.

Cartesian coordinates for DFT-optimized structure of $\mathbf{1}^{+}$:

Charge = 1 multiplicity = 1

C	-0.34880242	0.94042121	0.77191848
C	-1.75014753	0.93094294	0.78496869
C	0.35885386	-0.00007006	-0.00005069
C	0.53087003	1.84678154	1.51849746
C	-2.46148550	-0.00002491	-0.00026009
C	-0.34871420	-0.94053982	-0.77213045
N	1.87738064	1.62021108	1.33737319
C	0.10289389	2.88047195	2.36362491
Ru	2.34156496	-0.00002274	0.00002506
H	-2.31740547	1.63176722	1.38971468
C	-1.75005226	-0.93101114	-0.78538898
C	0.53104193	-1.84694277	-1.51856503
N	-3.87440724	-0.00001363	-0.00039543
C	2.76503530	2.39992339	1.98151616
C	1.03042249	3.67757749	3.02244248
N	1.87752720	-1.62031342	-1.33736991
N	4.40964395	0.00006140	-0.00001320
N	2.80535601	-1.31953761	1.59510437
N	2.80522273	1.31958536	-1.59508844
H	-0.96004136	3.05089204	2.49560225
C	2.39313033	3.43489594	2.83021268
C	0.10315592	-2.88074927	-2.36359689
C	2.76525679	-2.40006542	-1.98136151
C	-4.59923507	-1.22583352	-0.09119640
C	-4.59917941	1.22582684	0.09075577
C	5.06063179	-0.75772250	0.91370229
C	5.06054794	0.75790732	-0.91373243
C	4.14994071	-1.50025071	1.81276737
C	4.14978635	1.50036751	-1.81278481
C	1.92935920	-1.96956302	2.38429376
C	1.92916188	1.96956791	-2.38423347
H	-2.31724728	-1.63180077	-1.39023599
H	3.81062448	2.17328120	1.79964052
H	0.69774015	4.47777477	3.67692823
C	1.03075879	-3.67791994	-3.02223165
C	2.39344588	-3.43516879	-2.82993945
C	-4.27740729	2.31725951	-0.72369612
C	-5.66841440	1.35664089	0.99463663
C	-5.66884340	-1.35660493	-0.99464381
C	-4.27721240	-2.31728338	0.72314297
C	6.45880587	-0.77398606	0.93263009
C	6.45872273	0.77433255	-0.93264918
C	2.32427071	-2.81789749	3.41348808
C	4.60214974	-2.34194136	2.83343076
C	4.60192064	2.34205812	-2.83348358
C	2.32399476	2.81793326	-3.41343573
H	3.15323844	4.03111759	3.32342161
H	-0.95976461	-3.05121546	-2.49563422
H	3.81082354	-2.17333289	-1.79947141
H	0.88352384	-1.78808947	2.16444356
H	0.88334310	1.78802006	-2.16436469
C	-4.98498310	3.51876239	-0.63587645

C	-6.39079056	2.53890119	1.07188643
C	-6.39132264	-2.53882242	-1.07158956
C	-4.98489373	-3.51874450	0.63561352
C	7.15336958	0.00021535	-0.00000730
C	3.68691077	-3.00801330	3.64301050
C	3.68661739	3.00809126	-3.64302258
H	0.69815013	-4.47822180	-3.67662698
H	3.15360517	-4.03143502	-3.32301577
H	-3.46401003	2.22813506	-1.43794024
H	-5.93444778	0.51811520	1.63079954
H	-5.93508867	-0.51807859	-1.63071663
H	-3.46352896	-2.22821268	1.43706632
H	7.00410011	-1.37255634	1.65368172
H	7.00394765	1.37297436	-1.65369330
H	1.57329747	-3.31501751	4.01818823
H	5.66631007	-2.47428602	2.99358696
H	5.66606776	2.47442522	-2.99370729
H	1.57297745	3.31503593	-4.01809531
C	-6.05418202	3.63470958	0.26112938
C	-6.05445581	-3.63464460	-0.26096484
H	-4.70749938	4.34310484	-1.28303692
H	-7.22088307	2.64260646	1.76353898
H	-7.22169721	-2.64247395	-1.76291156
H	-4.70719398	-4.34309848	1.28266684
H	8.23850881	0.00028448	0.00000367
H	4.03238611	-3.66209737	4.43729859
H	4.03203186	3.66217693	-4.43733632
O	-6.82021747	4.75033042	0.42202032
O	-6.82060462	-4.75023542	-0.42155546
C	-6.55644986	5.87421894	-0.40279561
C	-6.55674848	-5.87403056	0.40335648
H	-5.54416437	6.26771917	-0.23836413
H	-7.28749484	6.63274606	-0.11830520
H	-6.68073296	5.63159959	-1.46644224
H	-5.54459380	-6.26774727	0.23863283
H	-7.28802921	-6.63247575	0.11925238
H	-6.68060871	-5.63120805	1.46700589

Cartesian coordinates for DFT-optimized structure of $\mathbf{1}^{2+}$:

Charge = 2 multiplicity = 2

C	-0.35738562	0.92943458	0.80347791
C	-1.74838310	0.93064507	0.80387627
C	0.35203039	-0.00047203	-0.00064143
C	0.52729428	1.81007632	1.58671560
C	-2.45122821	-0.00055049	-0.00149629
C	-0.35682796	-0.93041501	-0.80518533
N	1.86915478	1.58376907	1.39081533
C	0.10014992	2.80829171	2.46808282
Ru	2.30259430	-0.00030082	-0.00002806
H	-2.32112639	1.61043644	1.42644226
C	-1.74780828	-0.93163603	-0.80656573
C	0.52849819	-1.81081635	-1.58801809
N	-3.85947921	-0.00046885	-0.00180286
C	2.76123120	2.33651873	2.05850202
C	1.03295008	3.58027692	3.15430526
N	1.87021315	-1.58480737	-1.39072218
N	4.39744855	0.00004164	0.00017630
N	2.79203514	-1.36453278	1.56725529
N	2.79181226	1.36504234	-1.56596116
H	-0.96133894	2.97684481	2.61456009
C	2.39186370	3.34147705	2.94648546
C	0.10203474	-2.80850692	-2.47029005
C	2.76277549	-2.33777180	-2.05750401
C	-4.57939294	-1.21802016	-0.08883450
C	-4.57900582	1.21733619	0.08619736
C	5.04525218	-0.77871628	0.89218646
C	5.04516129	0.77687993	-0.89356749
C	4.13666063	-1.54414957	1.77689536
C	4.13641225	1.54514014	-1.77559942
C	1.92252120	-2.03518107	2.34527210
C	1.92214069	2.03840670	-2.34150955
H	-2.32009052	-1.61109883	-1.42989524
H	3.80581675	2.11589387	1.86646446
H	0.70524211	4.35520896	3.84030860
C	1.03535052	-3.58033136	-3.15600287
C	2.39409982	-3.34215432	-2.94643190
C	-4.16987846	2.34699924	-0.64555407
C	-5.73350600	1.30286034	0.89615415
C	-5.73407392	-1.30395779	-0.89856152
C	-4.17080352	-2.34710328	0.64419420
C	6.44401499	-0.79983928	0.91052656
C	6.44392429	0.79282544	-0.91656269
C	2.32397040	-2.90359343	3.35583010
C	4.59641034	-2.40433929	2.77734497
C	4.59590905	2.40923114	-2.77279346
C	2.32336192	2.91033019	-3.34910539
H	3.15461409	3.91781344	3.45863811
H	-0.95934566	-2.97684490	-2.61779745
H	3.80723347	-2.11793900	-1.86384940
H	0.87414818	-1.85712381	2.13707444
H	0.87380609	1.85965827	-2.13372174
C	-4.88784467	3.53445836	-0.57980156

C	-6.44671618	2.48212295	0.96860360
C	-6.44777358	-2.48299915	-0.96969510
C	-4.88924674	-3.53431365	0.57974724
C	7.13781140	-0.00481967	-0.00420065
C	3.68707529	-3.09207649	3.57675336
C	3.68641635	3.09983950	-3.56951991
H	0.70815953	-4.35467059	-3.84292084
H	3.15725227	-3.91848384	-3.45799222
H	-3.30290320	2.27995490	-1.29470290
H	-6.04885961	0.44280402	1.47715854
H	-6.04912599	-0.44444705	-1.48051358
H	-3.30385340	-2.27969846	1.29333972
H	6.98997430	-1.41649243	1.61509523
H	6.98981878	1.40694878	-1.62338841
H	1.57755596	-3.41614605	3.95300594
H	5.66116901	-2.53541952	2.93232412
H	5.66064819	2.54139560	-2.92700514
H	1.57679747	3.42495696	-3.94430789
C	-6.03859822	3.61422706	0.22879080
C	-6.04013829	-3.61446630	-0.22863591
H	-4.56631748	4.38276009	-1.17200760
H	-7.32728749	2.56765138	1.59631925
H	-7.32838913	-2.56887845	-1.59730326
H	-4.56792849	-4.38215426	1.17272929
H	8.22293898	-0.00701091	-0.00616134
H	4.03873412	-3.76048891	4.35607241
H	4.03788882	3.77127053	-4.34632067
O	-6.80936002	4.70274955	0.36387641
O	-6.81121114	-4.70288003	-0.36270794
C	-6.49138583	5.89402832	-0.36261798
C	-6.49415745	-5.89328531	0.36564843
H	-5.50528974	6.27686324	-0.07614762
H	-7.25885112	6.61645671	-0.08672437
H	-6.52638371	5.71440726	-1.44295051
H	-5.50856000	-6.27757695	0.07941979
H	-7.26246085	-6.61539460	0.09125804
H	-6.52855402	-5.71183022	1.44569092

Cartesian coordinates for DFT-optimized structure of $\mathbf{1}^{3+}$:

Charge =3 multiplicity = 3

C	-0.35665645	0.89342671	0.85154871
C	-1.75520041	0.88831903	0.85327264
C	0.32780589	0.00016404	0.00024610
C	0.53152657	1.74341662	1.67503268
C	-2.44368372	0.00021159	-0.00005108
C	-0.35645706	-0.89309557	-0.85124774
N	1.87403677	1.53320617	1.46753937
C	0.09933435	2.69305053	2.60077551
Ru	2.28938102	0.00010082	0.00039140
H	-2.33252629	1.53673071	1.50406753
C	-1.75494445	-0.88793354	-0.85324478
C	0.53177030	-1.74326022	-1.67470533
N	-3.87256474	0.00015607	-0.00020615
C	2.76525930	2.25440151	2.16548074
C	1.03307577	3.43760479	3.32349689
N	1.87429637	-1.53335685	-1.46714080
N	4.43682190	-0.00066323	-0.00030575
N	2.83818355	-1.41925116	1.50357440
N	2.83824576	1.42125150	-1.50110352
H	-0.96183062	2.85069437	2.75979381
C	2.39028491	3.21625240	3.10263785
C	0.09945667	-2.69276367	-2.60046599
C	2.76541485	-2.25472597	-2.16500589
C	-4.58554469	-1.21737473	-0.01909406
C	-4.58565556	1.21763273	0.01859609
C	5.08543774	-0.81226813	0.85717053
C	5.08547585	0.81006031	-0.85858284
C	4.17899522	-1.61231303	1.70918269
C	4.17906133	1.61205605	-1.70879004
C	1.95495650	-2.11189232	2.24789667
C	1.95504133	2.11639613	-2.24311657
H	-2.33216353	-1.53635207	-1.50412846
H	3.81107978	2.05032133	1.96321210
H	0.70275651	4.17688964	4.04645480
C	1.03311582	-3.43753253	-3.32315457
C	2.39033792	-3.21650510	-3.10221918
C	-4.15211771	2.32658302	-0.74212505
C	-5.77367310	1.32908535	0.78597579
C	-5.77351731	-1.32890730	-0.78653758
C	-4.15191792	-2.32632662	0.74157244
C	6.48410181	-0.83500212	0.87813341
C	6.48414123	0.83056618	-0.88159070
C	2.34871013	-3.02217826	3.22431054
C	4.62839096	-2.51442972	2.67498641
C	4.62848559	2.51421410	-2.67454103
C	2.34882138	3.02678026	-3.21942867
H	3.15101129	3.77148629	3.64047633
H	-0.96172090	-2.85020932	-2.75958508
H	3.81126034	-2.05086525	-1.96263719
H	0.90781585	-1.92194824	2.04633106
H	0.90789189	1.92828980	-2.03987494
C	-4.88254400	3.50259788	-0.75914532

C	-6.49747904	2.49921258	0.78211961
C	-6.49721027	-2.49910296	-0.78276615
C	-4.88222657	-3.50241502	0.75849869
C	7.17847751	-0.00281661	-0.00227894
C	3.70952261	-3.22802220	3.44226182
C	3.70963859	3.23020107	-3.43960727
H	0.70265995	-4.17673359	-4.04613741
H	3.15098072	-3.77190336	-3.64000394
H	-3.26114136	2.24318644	-1.35603494
H	-6.09823052	0.49595393	1.39988210
H	-6.09813040	-0.49577977	-1.40041975
H	-3.26095875	-2.24288673	1.35550258
H	7.02899525	-1.47954976	1.55791807
H	7.02906701	1.47438389	-1.56204060
H	1.59680778	-3.55330691	3.79767112
H	5.69130142	-2.65926074	2.82967306
H	5.69139842	2.65728969	-2.83083627
H	1.59693266	3.55990079	-3.79095513
C	-6.07379227	3.60410820	0.00015166
C	-6.07344396	-3.60399741	-0.00083874
H	-4.54962808	4.33005029	-1.37413806
H	-7.39592464	2.60793435	1.38024901
H	-7.39562221	-2.60788209	-1.38093567
H	-4.54923766	-4.32987403	1.37344321
H	8.26380565	-0.00368420	-0.00307553
H	4.05330380	-3.92980063	4.19544570
H	4.05343828	3.93202955	-4.19273594
O	-6.85458288	4.67617356	0.05471961
O	-6.85411895	-4.67614088	-0.05549712
C	-6.54736405	5.85751832	-0.70913580
C	-6.54680312	-5.85749747	0.70830304
H	-5.58460362	6.27552458	-0.39853351
H	-7.34738173	6.56009007	-0.48186315
H	-6.54389079	5.63014054	-1.77964300
H	-5.58399036	-6.27538748	0.39770784
H	-7.34674216	-6.56013775	0.48096583
H	-6.54338681	-5.63017912	1.77882307

Cartesian coordinates for DFT-optimized structure of **2**$^{+}$:

Charge = 1 multiplicity = 1

C	-0.28615612	1.13405794	-0.31006911
C	-1.67636181	1.16788236	-0.32515112
N	0.37518627	-0.00125563	-0.00131435
C	0.62429009	2.26491025	-0.61664970
C	-2.40904750	-0.00194979	-0.00235502
C	-0.28584124	-1.13694616	0.30673553
N	1.97066698	1.99701215	-0.54456104
C	0.16818526	3.54098040	-0.95823248
Ru	2.45739296	-0.00060950	0.00004082
H	-2.21015842	2.07175579	-0.58605674
C	-1.67603049	-1.17153273	0.32064214
C	0.62490559	-2.26734847	0.61410186
C	2.84146125	2.98880817	-0.81165612
C	1.07853963	4.55766664	-1.23234469
N	1.97120401	-1.99864084	0.54371438
C	4.43221304	0.00000532	0.00168145
N	2.90690858	-0.55283072	-2.02660289
N	2.90315592	0.55199631	2.02738605
N	-3.79282129	-0.00149962	-0.00229979
H	-0.89700505	3.73693263	-1.00710414
C	2.44196454	4.27552188	-1.15790725
C	0.16912437	-3.54378930	0.95473568
C	2.84225479	-2.99005699	0.81137202
C	5.13570418	-0.32450782	-1.17813916
C	5.13350805	0.32474488	1.18275038
C	4.25305836	-0.63244739	-2.30837246
C	4.24877892	0.63231083	2.31145569
C	2.01860882	-0.81446122	-3.00308762
C	2.01304980	0.81336846	3.00229268
C	-4.54048460	-1.22853480	-0.03921015
C	-4.53762694	1.22736938	0.03707863
H	-2.20948513	-2.07591544	0.58040470
H	3.88911110	2.72007425	-0.73938938
H	0.72819609	5.55013392	-1.49795960
C	1.07974458	-4.56006782	1.22948828
C	2.44309205	-4.27713325	1.15666324
C	6.53916127	-0.32321700	-1.17174741
C	6.53697006	0.32396533	1.17882800
C	2.38871545	-1.16632630	-4.29501555
C	4.67925592	-0.98417227	-3.59717459
C	4.67258860	0.98444193	3.60093430
C	2.38076164	1.16562338	4.29479510
C	-4.38670316	2.12281958	1.10855227
C	-5.45531382	1.52550043	-0.97232900
C	-5.47152559	-1.51440250	0.96155368
C	-4.37950381	-2.13478134	-1.10017030
H	3.19044521	5.03373276	-1.36216656
H	-0.89600960	-3.74035788	1.00237366
H	3.88983504	-2.72070468	0.74041240
H	0.97359660	-0.73380536	-2.72173649
H	0.96856704	0.73213984	2.71915448
C	7.22649780	0.00049683	0.00414653

C	3.75084948	-1.25254283	-4.59493714
C	3.74233640	1.25252996	4.59705420
C	-5.12552883	3.29671267	1.15349507
C	-6.21535036	2.69563756	-0.92675131
C	-6.23464009	-2.68257720	0.91773554
C	-5.12123151	-3.30691877	-1.14281605
H	0.72965906	-5.55282790	1.49434730
H	3.19176873	-5.03500666	1.36145607
H	7.11017522	-0.56884626	-2.06432354
H	7.10632514	0.56977011	2.07241396
H	1.62765876	-1.36595396	-5.04175942
H	5.74188087	-1.04367689	-3.80646733
H	5.73482360	1.04451892	3.81203360
H	1.61832285	1.36501256	5.04019169
H	-3.68998281	1.89075423	1.90925279
H	-5.58733666	0.83136148	-1.79683040
H	-5.61172740	-0.81216068	1.77776692
H	-3.67225839	-1.91289326	-1.89448649
C	-6.05039094	3.59358900	0.13722879
C	-6.05949755	-3.59129798	-0.13534172
H	8.31225119	0.00068798	0.00510650
H	4.08216659	-1.52457111	-5.59275491
H	4.07180123	1.52488637	5.59539566
H	-5.02073299	3.99485088	1.97777602
H	-6.92377269	2.89650537	-1.72170236
H	-6.95338011	-2.87352237	1.70583576
H	-5.00842397	-4.01317754	-1.95908873
O	-6.72781032	4.76053575	0.28073326
O	-6.73881715	-4.75754522	-0.27600524
C	-7.69978081	5.11021188	-0.69789589
C	-7.72342773	-5.09499039	0.69422046
H	-7.24524782	5.22872907	-1.68974968
H	-8.11616959	6.06505391	-0.37456541
H	-8.50120377	4.36259491	-0.75065434
H	-7.28119827	-5.20493397	1.69260380
H	-8.13856072	-6.05186179	0.37529184
H	-8.52336725	-4.34477355	0.72997557

Cartesian coordinates for DFT-optimized structure of $\mathbf{2}^{2+}$:

Charge = 2 multiplicity = 2

C	0.28302395	-1.12480223	-0.38258257
C	1.66397744	-1.15857914	-0.39199723
N	-0.37855459	0.00001144	-0.00006947
C	-0.62869541	-2.23602481	-0.76797618
C	2.39897760	0.00000561	-0.00001785
C	0.28301442	1.12481649	0.38248583
N	-1.97337842	-1.97610311	-0.67652248
C	-0.17471616	-3.48405951	-1.19662411
Ru	-2.42739809	-0.00000574	-0.00004057
H	2.20161822	-2.04130797	-0.71010515
C	1.66396726	1.15858889	0.39194501
C	-0.62871258	2.23603592	0.76786997
C	-2.85056038	-2.93937862	-1.00486239
C	-1.09158402	-4.47763789	-1.53763912
N	-1.97339391	1.97610607	0.67641575
C	-4.44208236	-0.00003408	0.00011888
N	-2.92125292	0.67243619	-1.97994708
N	-2.92092862	-0.67250358	1.97994065
N	3.77044338	0.00001762	-0.00001253
H	0.88889794	-3.68243865	-1.26370508
C	-2.45331594	-4.20173634	-1.43987747
C	-0.17474098	3.48407683	1.19650798
C	-2.85058145	2.93938191	1.00473966
C	-5.13869636	0.39627691	-1.15391789
C	-5.13850741	-0.39634309	1.15426868
C	-4.25968689	0.77467592	-2.26363284
C	-4.25931746	-0.77474722	2.26383857
C	-2.01427440	0.99169302	-2.92357078
C	-2.01380324	-0.99179110	2.92341272
C	4.51863405	1.22447149	-0.03229716
C	4.51866479	-1.22441995	0.03226914
H	2.20160172	2.04131483	0.71007316
H	-3.89750861	-2.67472186	-0.91062264
H	-0.74418633	-5.44969793	-1.87286874
C	-1.09161476	4.47765419	1.53751004
C	-2.45334490	4.20174598	1.43974327
C	-6.54301649	0.39519973	-1.15027887
C	-6.54282805	-0.39526629	1.15085939
C	-2.37438552	1.42834594	-4.19125945
C	-4.67461248	1.21056979	-3.52817444
C	-4.67404413	-1.21066292	3.52843812
C	-2.37371412	-1.42846955	4.19114932
C	4.26668889	-2.19311734	1.02158173
C	5.54358492	-1.43835473	-0.89793168
C	5.54369430	1.43834158	0.89776456
C	4.26647771	2.19326061	-1.02147488
H	-3.20244333	-4.94389681	-1.69337929
H	0.88887182	3.68246294	1.26358830
H	-3.89752788	2.67471832	0.91050050
H	-0.97248691	0.88793923	-2.64031200
H	-0.97205955	-0.88804019	2.63999301
C	-7.23177925	-0.00003293	0.00034673

C	-3.73356340	1.53944595	-4.49647229
C	-3.73284337	-1.53956482	4.49657934
C	5.01499132	-3.35693508	1.06170585
C	6.30035363	-2.60547531	-0.86205265
C	6.30042984	2.60548284	0.86187852
C	5.01474514	3.35710024	-1.06160325
H	-0.74422293	5.44971920	1.87273135
H	-3.20247690	4.94390576	1.69323347
H	-7.10890440	0.69623029	-2.02773275
H	-7.10857298	-0.69629832	2.02840474
H	-1.60700855	1.67286239	-4.91734759
H	-5.73439460	1.28836186	-3.74356684
H	-5.73379245	-1.28845582	3.74399620
H	-1.60622207	-1.67300847	4.91710830
H	3.50083534	-2.01681076	1.77133765
H	5.74679804	-0.68952816	-1.65696545
H	5.74704236	0.68944872	1.65669674
H	3.50051271	2.01700822	-1.77112968
C	6.04152071	-3.57927314	0.11991304
C	6.04141752	3.57937122	-0.11995044
H	-8.31693245	-0.00003346	0.00043535
H	-4.05347212	1.87744233	-5.47727991
H	-4.05259734	-1.87757969	5.47743105
H	4.84739276	-4.10677611	1.82764103
H	7.08313606	-2.75087572	-1.59657091
H	7.08332482	2.75083006	1.59628731
H	4.84700716	4.10701187	-1.82743879
O	6.70820493	-4.73819155	0.25035914
O	6.70805026	4.73831994	-0.25038557
C	7.79457603	-5.02991112	-0.63464143
C	7.79453793	5.02999009	0.63448855
H	7.45065035	-5.08892130	-1.67359869
H	8.17421298	-6.00143834	-0.31957704
H	8.58673617	-4.27832208	-0.54400501
H	7.45076100	5.08887259	1.67350218
H	8.17408709	6.00156778	0.31947405
H	8.58671670	4.27844456	0.54365451

Cartesian coordinates for DFT-optimized structure of $\mathbf{2}^{3+}$:

Charge = 3 multiplicity = 3

C	0.28502595	-1.06785154	-0.50376335
C	1.67999921	-1.09969052	-0.51888708
N	-0.36659386	-0.00001704	0.00002204
C	-0.62389084	-2.12166858	-1.01447550
C	2.39133814	-0.00000250	-0.00003228
C	0.28503476	1.06782504	0.50377957
N	-1.96533885	-1.86461350	-0.89236140
C	-0.17677319	-3.31231920	-1.58824852
Ru	-2.50768082	-0.00003108	0.00006991
H	2.22064577	-1.93858801	-0.93816353
C	1.68000827	1.09967967	0.51884585
C	-0.62387260	2.12163302	1.01452684
C	-2.84902407	-2.77967573	-1.33340079
C	-1.09708075	-4.25518165	-2.04517812
N	-1.96532270	1.86456042	0.89247320
C	-4.45078487	-0.00003440	0.00011862
N	-2.91545431	0.91245415	-1.91986739
N	-2.91535584	-0.91252231	1.92002635
N	3.80558618	0.00001333	-0.00006889
H	0.88565560	-3.50666586	-1.68105211
C	-2.45661006	-3.98356832	-1.91440594
C	-0.17674431	3.31229186	1.58827444
C	-2.84899964	2.77961401	1.33354718
C	-5.14002058	0.53230659	-1.11888309
C	-5.13996334	-0.53237669	1.11915489
C	-4.25724906	1.03824446	-2.18518008
C	-4.25713709	-1.03831381	2.18540709
C	-2.02608159	1.34023532	-2.83004718
C	-2.02593674	-1.34030872	2.83015841
C	4.52299192	1.19379888	-0.24239589
C	4.52304216	-1.19375039	0.24222146
H	2.22066314	1.93858652	0.93809335
H	-3.89607749	-2.53038264	-1.21268962
H	-0.75559177	-5.18249442	-2.49382609
C	-1.09704328	4.25514489	2.04524070
C	-2.45657493	3.98351400	1.91452977
C	-6.53693010	0.52864096	-1.11043691
C	-6.53687332	-0.52871596	1.11077757
C	-2.40224337	1.91208516	-4.04319884
C	-4.69243317	1.60469023	-3.38513681
C	-4.69226008	-1.60476269	3.38538456
C	-2.40203674	-1.91216246	4.04332738
C	4.10788784	-2.09961858	1.24957994
C	5.69071446	-1.47740103	-0.50415596
C	5.69070435	1.47747963	0.50390731
C	4.10773536	2.09966710	-1.24971152
H	-3.21107328	-4.68520466	-2.25354954
H	0.88568618	3.50665248	1.68102928
H	-3.89605521	2.53030761	1.21288271
H	-0.97991465	1.21635455	-2.57130867
H	-0.97978290	-1.21643015	2.57136565
C	-7.21670876	-0.00003872	0.00018709

C	-3.76111385	2.04636018	-4.32400626
C	-3.76089287	-2.04643616	4.32420475
C	4.84134852	-3.23651742	1.50301055
C	6.42864657	-2.62121708	-0.25823576
C	6.42858127	2.62132348	0.25795102
C	4.84114070	3.23659368	-1.50317797
H	-0.75554597	5.18246415	2.49386892
H	-3.21103195	4.68514270	2.25370295
H	-7.11608031	0.92348877	-1.93968804
H	-7.11598130	-0.92356627	1.94005694
H	-1.64391456	2.24081152	-4.74532292
H	-5.75416418	1.69875264	-3.58425124
H	-5.75398093	-1.69882532	3.58455316
H	-1.64367224	-2.24089297	4.74541096
H	3.23619562	-1.87591286	1.85612944
H	5.99512922	-0.80507503	-1.29937820
H	5.99519495	0.80515469	1.29910150
H	3.23600560	1.87594186	-1.85620034
C	6.01812282	-3.51796293	0.75658223
C	6.01795767	3.51806828	-0.75682772
H	-8.30234558	-0.00004069	0.00021392
H	-4.09372871	2.48688990	-5.25869048
H	-4.09346002	-2.48696835	5.25890478
H	4.55998336	-3.92707246	2.29089646
H	7.30591783	-2.82888159	-0.85908847
H	7.30588603	2.82901023	0.85874709
H	4.55969645	3.92715067	-2.29103394
O	6.64634332	-4.63684393	1.08620883
O	6.64611694	4.63697549	-1.08648193
C	7.87711620	-5.01688879	0.43409499
C	7.87692120	5.01705417	-0.43444712
H	7.70538024	-5.18755937	-0.63295327
H	8.17883740	-5.94508514	0.91604314
H	8.64099139	-4.24893526	0.58704672
H	7.70525229	5.18770425	0.63261521
H	8.17857710	5.94526760	-0.91640327
H	8.64081258	4.24912928	-0.58746159

EPR measurement:

The EPR measurement of $\mathbf{1}^{2+}$ (as-prepared sample) was performed in a solution in acetonitrile at room temperature on a Bruker ELEXSYS E500-10/12 spectrometer. The spectrometer frequency ν is 9.51×10^9 Hz.