Electronic supplementary information for manuscript:

Mn(IV) and Mn(V)-radical Species Supported by the Redox Non-innocent bis(2-amino-3,5-di-*tert*-butylphenyl)amine Pincer Ligand

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Content:

I. Experimental section

I.1. Materials and methods

All operations were performed under anaerobic conditions under a pure argon atmosphere using standard Schlenk techniques. Anhydrous toluene and triethylamine were distilled over CaH_2 under an argon atmosphere prior to use. Anhydrous dichloromethane, acetonitrile, methanol were purchased from Acros. High-pressure reactions were carried out using a 0.6 L Parr Instrument stainless steel vessel. The syntheses of 3,5-di-*tert*-butyl-2-nitrobromobenzene **4** and 3,5-di-*tert*-butyl-2-nitrobenzoïc acid were reported elsewhere.[1-3] All other chemicals were purchased from Acros, Alfa-Aesar, Sigma-Aldrich or TCI and were used as received. NMR spectra were recorded on a Brüker Avance 300, 400 or 500 (^{1}H at 300, 400 or 500 MHz, ^{13}C at 75, 100 or 125 MHz). Chemical shifts are given relative to solvent residual peaks. Mass spectra were recorded on a Bruker Esquire 3000 (ESI/Ion Trap) equipment. Microanalysis were performed by using an apparatus designed by the Service Central d'Analyse du CNRS (Lyon, France). UV/Vis visible spectra were recorded on a Perkin-Elmer Lambda 1050 spectrophotometer in quartz cells (Hellma) of 1.00 mm path length. X-band EPR spectra were recorded on an EMX plus spectrometer equipped with an Oxford Helium cryostat. Spectra were treated using the Bruker SIMFONIA or Easyspin 4.5.5 software. Electrochemical measurements were carried out using a BioLogic SP300 potentiostat. Experiments were performed in a standard three-electrode cell under argon atmosphere in CH_2Cl_2 solutions containing 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. An $Ag/AgNO_3$ (0.01 M) reference electrode was used. All the potentials given in the text are referred to the regular Fc^+/Fc redox couple used as an internal reference. A glassy carbon disc electrode (5 mm diameter), which was polished with 1 mm diamond paste, was used as the working electrode. RDE experiments were performed by using a Radiometer CTV101 unit. Electrolysis was conducted at constant applied potential by using a EG&G PAR 273A potentiostat and a carbon plate as working electrode.

I.2. Crystal structure analysis

Crystals were mounted on a Kappa CCD Nonius diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and a cryostream cooler. The collected reflections were corrected for absorption (SADABS). Crystal structural solution (direct method) and refinement (by full-matrix least squares on F) was performed using the OLEX 2

analysis package.[4] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generated in idealized positions, riding on the carrier atoms, with isotropic thermal parameters.

Crystallographic data and structure refinement for complexes 2 and 2^{2+}

	2, 0.29 C_6H_6	$\mathbf{2^{2+}}$ **• 2 $\mathbf{SbF_6}$**, C_5H_{12}
Empirical formula	$C_{57.74}H_{85.74}MnN_6$	$C_{61}H_{96}F_{12}MnN_6Sb_2$
Formula weight	918.93	1439.88
Temperature/K	200	200
Crystal system	orthorhombic	monoclinic
Space group	$C222_1$	C2/c
a/Å	19.543(4)	15.525(3)
b/Å	24.165(5)	33.075(7)
c/Å	23.605(5)	16.286(3)
α/°	90.00	90.00
β/°	90.00	118.46(3)
γ/°	90.00	90.00
Volume/$Å^3$	11148(4)	7352(3)
Z	8	4
$\rho_{calc}mg/mm^3$	1.095	1.301
m/mm^{-1}	0.277	0.966
F(000)	3994.0	2956.0
Crystal size/mm^3	0.71 × 0.55 × 0.1	0.42 × 0.26 × 0.21
2Θ range for data collection	3.78 to 50°	4.74 to 59.98°
Index ranges	$-23 \le h \le 22$, $-28 \le k \le 28$, $-28 \le l \le 27$	$-21 \le h \le 21$, $-45 \le k \le 46$, $-22 \le l \le 22$
Reflections collected	35850	58625
Independent reflections	9441[R(int) = 0.0324]	10701[R(int) = 0.0345]
Data/restraints/parameters	9441/196/679	10701/389/566
Goodness-of-fit on F^2	1.110	1.147
Final R indexes [I>=2σ (I)]	$R_1 = 0.0446$, $wR_2 = 0.1005$	$R_1 = 0.0447$, $wR_2 = 0.1192$
Final R indexes [all data]	$R_1 = 0.0659$, $wR_2 = 0.1120$	$R_1 = 0.0746$, $wR_2 = 0.1534$
Largest diff. peak/hole / e $Å^{-3}$	0.34/-0.27	0.86/-1.45
Flack parameter	-0.014(16)	

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1406874 and 1406875 (for **2** and $\mathbf{2^{2+}}$, respectively). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033) or via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

I.3. Magnetic measurements.

The temperature dependence of the magnetic susceptibility was measured in the temperature range 2-350 K on a powder sample of $\mathbf{2}^{2+}$ • 2 SbF_6^- in a applied magnetic field of 0.1 T using a SQUID magnetometer from Quantum Design model MPMS-XL. Magnetization versus magnetic field (0-0.5 T) was measured at 2 K. All data were corrected for the contribution of the sample holder and diamagnetism of the samples estimated from Pascal's constants.[5]

Fitting of the magnetic susceptibility. The Van Vleck equation for the temperature dependence of the magnetic susceptibility (χ_{vv}) modelling the magnetic interaction between a Mn(V) metal ion (S_{Mn}=1) and one radical (S_{rad}=1/2) and accordingly to the spin Hamiltonian $\hat{H} = -2J\hat{S}_{Mn}.\hat{S}_{rad}$ was first derivate using the Kambe approach: [6]

$$\chi_{vv} = \frac{0.375}{T} g^2 \frac{e^{(-3J/kT)} + 10}{4e^{(-3J/kT)} + 8}$$

$$\chi_{vv} = \frac{1.5}{T} \frac{e^{(-3J/kT)} + 10}{4e^{(-3J/kT)} + 8} \quad (\text{for } g = 2)$$

Then for fitting the experimental temperature dependence of the magnetic susceptibility, intermolecular interactions (z'J') were incorporated in the equation of the magnetic susceptibility (χ_{fit}) within the molecular field approximation using the well-known equation of Ginsberg and Lines: [7]

$$\chi_{fit} = \frac{\chi_{vv}}{1 - (2z'J'\chi_{vv} / Ng^2\beta^2)}$$

For z'J' expressed in wavenumber (cm^{-1}) this becomes:

$$\chi_{fit} = \frac{\chi_{vv}}{1 - (2z'J'\chi_{vv} / 0.26g^2)}$$

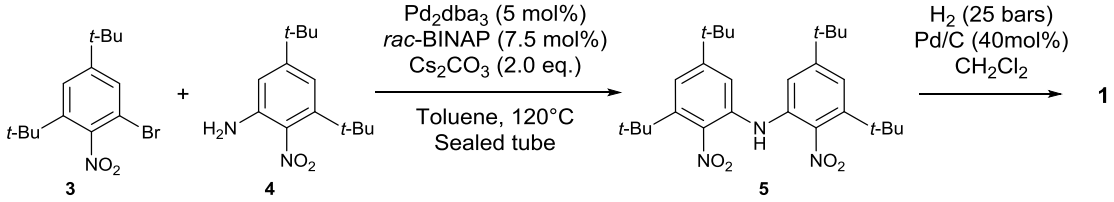
The equation was entered as a fitting function of Origin® software. During the fitting process J, z'J' and g were left riding as free variables (χ_{fit} and χ_{vv}) to give J =-262(2) cm^{-1}; z'J'=-0.68(7) cm^{-1} and g=2.02(2).

I.4. DFT Calculations.

Geometry optimization calculations were completed using the Gaussian 09 program (Revision D.01),[8] the B3LYP functional,[9, 10] and the 6-31G(d) basis set with a polarized continuum model (PCM) for CH_2Cl_2 (dielectric ε = 8.94).[11-14] Broken-symmetry[15-17] (BS) DFT calculations were performed with the same functional and basis sets. Frequency calculations at the same level of theory confirmed that the optimized structures were located at a minimum on the potential energy surface. Single-point calculations were performed using the BP86 functional, and the 6-311G(d) basis set with a PCM for CH_2Cl_2.[18, 19]

I.5 Synthetic procedures

Preparation of the ligand (1):



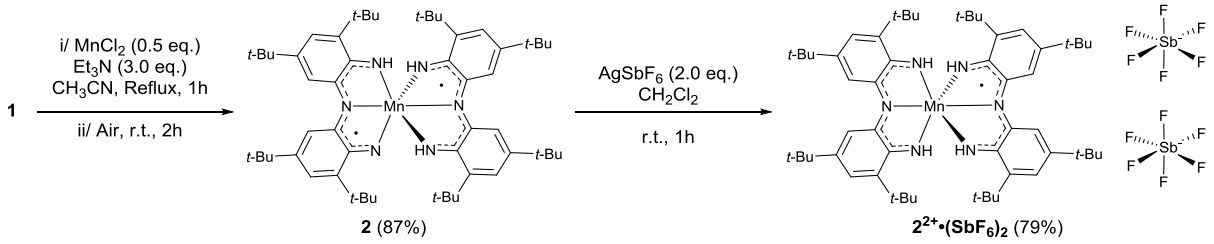
Bis(2-amino-3,5-di-*tert*-butylphenyl)amine (1). In a Paar pressure vessel, Pd/C (6.905 g (10% Pd, 50% wet), 3.24 mmol, 40 mol%) was added to a solution of the dinitro compound (3.92 g, 8.11 mmol, 1.0 eq.) in CH_2Cl_2 (90 mL). The resulting suspension was stirred at r.t. under H_2 (25 bars) during 24 hours. After complete consumption of the material (TLC monitoring) the mixture was filtrated through celite and abundantly washed with CH_2Cl_2. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The remaining residue was purified by column chromatography on silica gel (Eluent: CH_2Cl_2/pentane; 6:4, v:v then CH_2Cl_2 then CH_2Cl_2/MeOH; 96:4, v:v) to afford a white solid. Yield: 88 %. 1H NMR (500 MHz, CD_3OD): δ (ppm)= 6.99 (d, *J*= 2.3 Hz, 2H), 6.66 (d, *J*= 2.3 Hz, 2H), 1.45 (s, 18H), 1.2 (s, 18H). ^{13}C NMR (125 MHz, CD_3OD): δ (ppm)= 142.0, 135.4, 135.2, 134.1, 118.0, 116.6, 35.6, 35.1, 32.1, 30.5. MS (ESI): m/z= 424.4 $[M+H]^+$. IR: ν (cm^{-1}) 3471, 3332, 2952, 2898, 2870, 1568, 1477, 1420. Anal. Calcd for $C_{28}H_{45}N_3$: C, 79.38; H, 10.71; N, 9.92. Found: C, 79.38; H, 10.94; N, 9.63.

3,5-Di-*tert*-butyl-2-nitroaniline (4). At 5°C NaN_3 (3.94 g, 0.06 mol, 1.2 eq.) was added in small portions over 1.5 hour to a solution of 3,5-di-*tert*-butyl-2-nitrobenzoïc acid (14.17 g, 0.05 mol) in conc. H_2SO_4 (96 mL). The resulting mixture was stirred 12 hours at 0°C, then

heated to 70°C during 5 hours before being poured into an ice/water mixture. The yellow precipitate was filtrated, washed with water and dissolved in CH_2Cl_2. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The remaining yellow residue was purified by column chromatography on silica gel (Eluent: Pentane/CH_2Cl_2 ; 3:1 then 1:1, v:v) to give a yellow solid. Yield: 48%; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm)= 6.93 (d, *J*= 1.8 Hz, 1H), 6.67 (d, *J*= 1.8 Hz, 1H), 3.95 (br s, 2H), 1.38 (s, 9H), 1.28 (s, 9H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm)= 153.9, 142.4, 138.8, 138.0, 115.7, 112.8, 36.2, 35.1, 31.2. HRMS (ESI, $[M+H]^+$): m/z calcd for $C_{14}H_{23}N_2O_2$ 251.1759, found 251.1762. IR: ν (cm^{-1}) 3446, 3370, 2952, 2908, 2867, 1635, 1597, 1511, 1359.

Bis(2-nitro-3,5-di-*tert*-butylphenyl)amine (5). In a flame-dried sealed tube under argon, to a stirred suspension of Pd_2dba_3 (32 mg, 0.035 mmol, 5 mol%) and *rac*-BINAP (33 mg, 0.053 mmol, 7.5 mol%) in degassed toluene (2.8 mL) were added the aniline **4** (175 mg, 0.7 mmol, 1.0 eq.), the bromoarene **3** (264 mg, 0.84 mmol, 1.2 eq.) and cesium carbonate (456 mg, 1.4 mmol, 2.0 eq.). The resulting mixture was heated at 120°C during 24 hours. After cooling to r.t. the solution was filtrated on celite and the pad was abundantly washed with CH_2Cl_2. The filtrate was then concentrated under reduced pressure and the remaining residue was purified by flash chromatography on silica gel (Pentane/CH_2Cl_2 ; 75:25 to 6:4) to give an red-orange solid (335 mg, yield: 99%). Orange crystals were obtained by slow evaporation of a CH_2Cl_2/EtOH solution. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 7.18 (d, *J*= 2.0 Hz, 2H), 7.11 (d, *J*= 2.0 Hz, 2H), 6.53 (br s, 1H), 1.42 (s, 18H), 1.25 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)= 153.7, 142.7, 141.9, 134.8, 119.3, 115.5, 36.4, 35.4, 31.21, 31.16. MS (ESI): m/z= 482 $[M-H^+]^-$. IR: ν (cm^{-1}) 3383, 2958, 2870, 1575, 1486, 1473, 1363, 1239. Anal. Calcd for $C_{28}H_{41}N_3O_4$: C, 69.53; H, 8.54; N, 8.69. Found: C, 69.28; H, 8.79; N, 8.71.

Preparation of the complexes (2) and (2^{2+}):



(2). Under argon and at r.t., $MnCl_2$ (15 mg, 0.12 mmol, 0.5 eq.) and Et_3N (66 µL, 0.47 mmol, 2.0 eq.) were added to a degassed solution of H_3L (100 mg, 0.24 mmol, 1.0 eq.) in CH_3CN (5 mL). The resulting mixture was stirred at 80°C during 1 hour and turned rapidly from colorless to black. The reaction was then cooled to r.t. and exposed to air during 1 hour. The deep dark purple precipitate that formed was filtrated through a frit and abundantly washed with CH_3CN. Yield: 87 %. Suitable crystals for X-ray analysis were obtained under argon by slow diffusion of CH_3CN in a benzene solution. MS (ESI): m/z= 896.5 $[M+H]^+$. IR: ν (cm^{-1}) 3420, 2950, 2903, 2864, 1455, 1357, 1186. Anal. Calcd for $C_{56}H_{84}N_6Mn$, H_2O: C, 73.65; H, 9.38; N, 9.20. Found: C, 73.73; H, 9.53; N, 8.85.

$[2^{2+}](SbF_6)_2$. Under argon and at r.t., $AgSbF_6$ (20 mg, 0.056 mmol, 2.0 eq.) was added to a solution of **2** (25 mg, 0.028 mmol, 1.0 eq.) in dry CH_2Cl_2 (2.5 mL). The resulting mixture was stirred during 1 hour and filtrated through a frit. The filtrate was concentrated under reduced pressure. A black precipitate formed after the addition of pentane in a concentrated solution in CH_2Cl_2 and was isolated by filtration. Yield: 79 %. Suitable crystals for X-ray analysis were obtained by slow diffusion at r.t. of pentane in a concentrated solution of the product in 1,2-dichloroethane. MS (ESI): m/z= 488 $[M-2(SbF_6)]^{2+}$, 1130.5 $[M-SbF_6]^+$. IR: ν (cm^{-1}) 3348, 2956, 2873, 1584, 1464, 1443, 1363, 1108. Anal. Calcd for $C_{56}H_{84}N_6Mn \bullet 2\ (SbF_6)$, 0.5 CH_2Cl_2: C, 48.12; H, 6.08; N, 5.96. Found: C, 48.28; H, 6.16; N, 5.69.

II. Figures

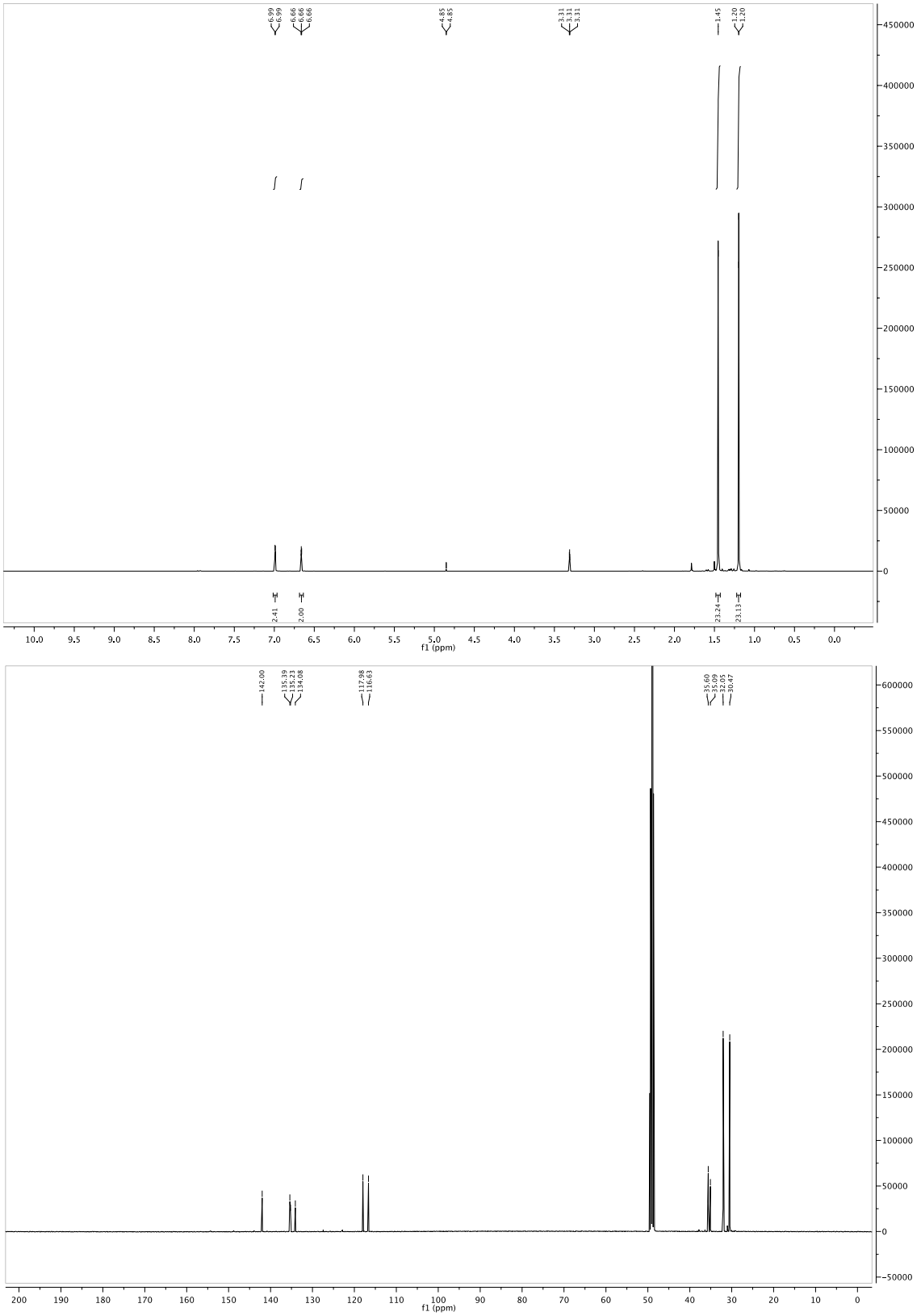


Figure S1. ^{1}H and ^{13}C NMR spectra of compound **1**.

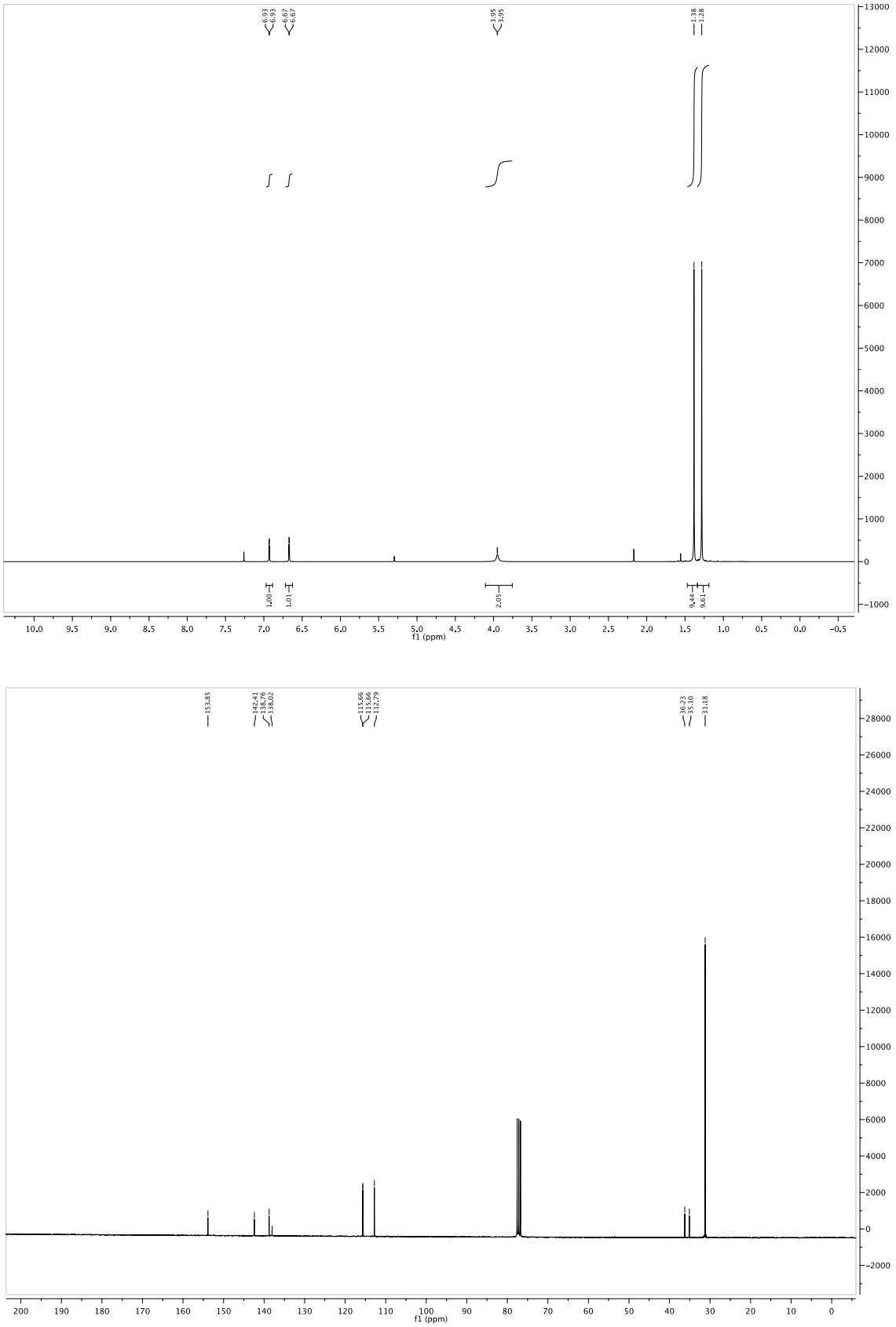


Figure S2. ^{1}H and ^{13}C NMR spectra of compound **4**.

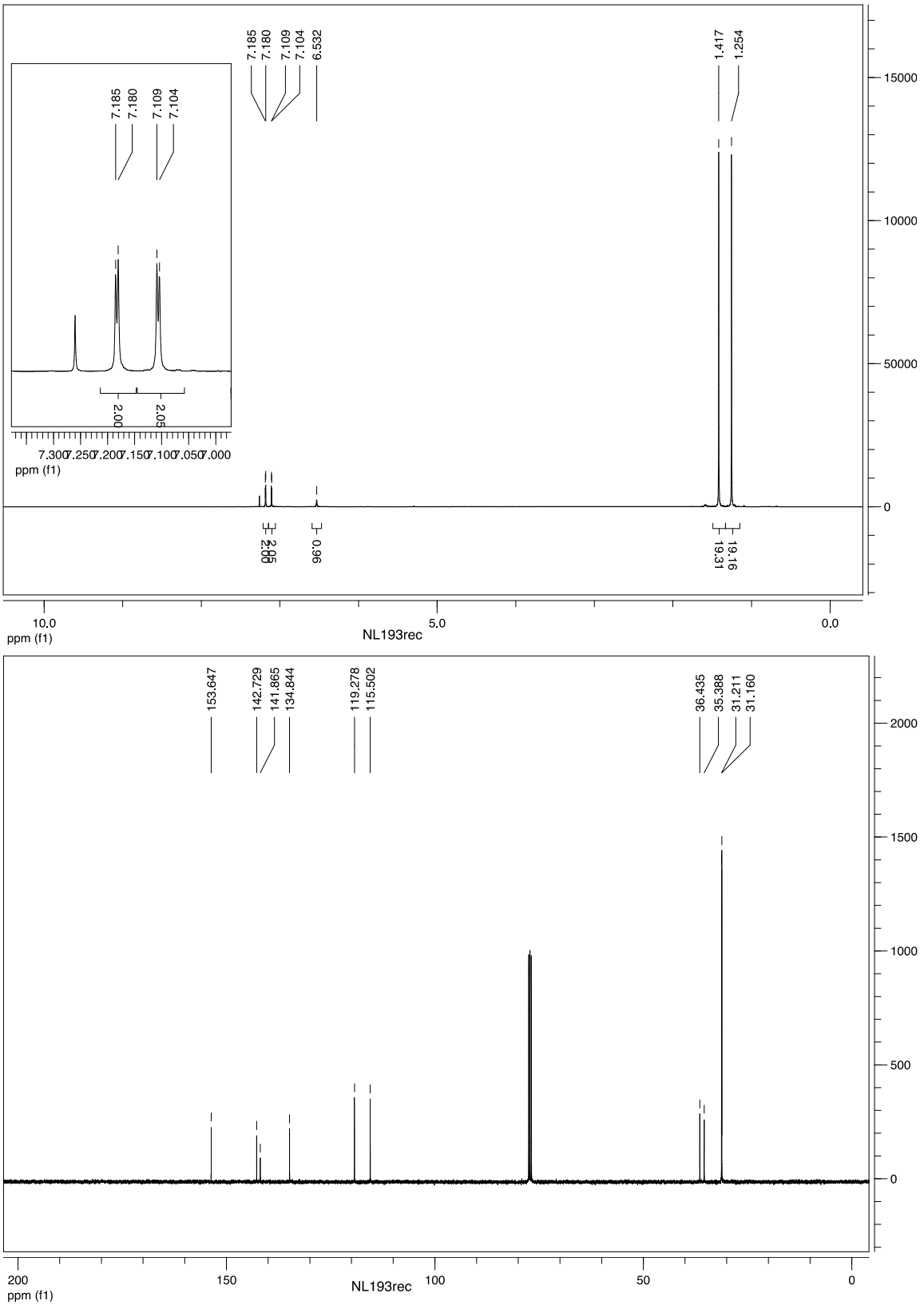


Figure S3. ^{1}H and ^{13}C NMR spectra of compound **5**.

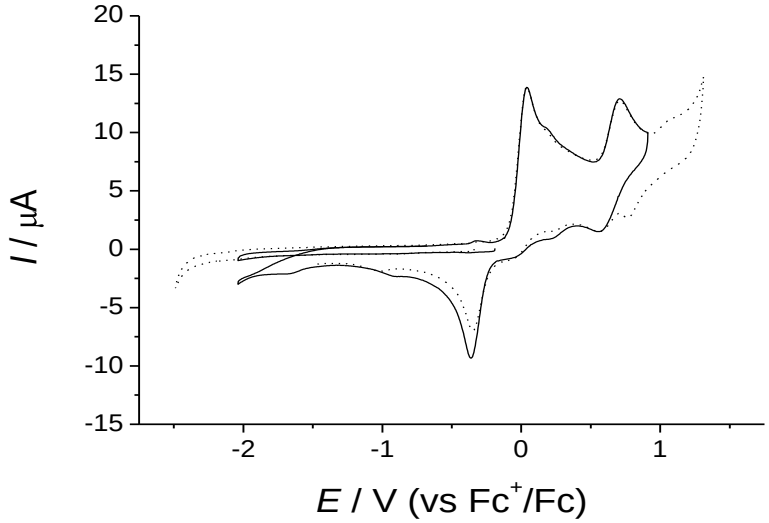


Figure S4. CV curve of a 1 mM CH_2Cl_2 (+0.1 M TBAP) solution of **1**. *T* = 298 K, scan rate = 0.1 V s^{-1}.

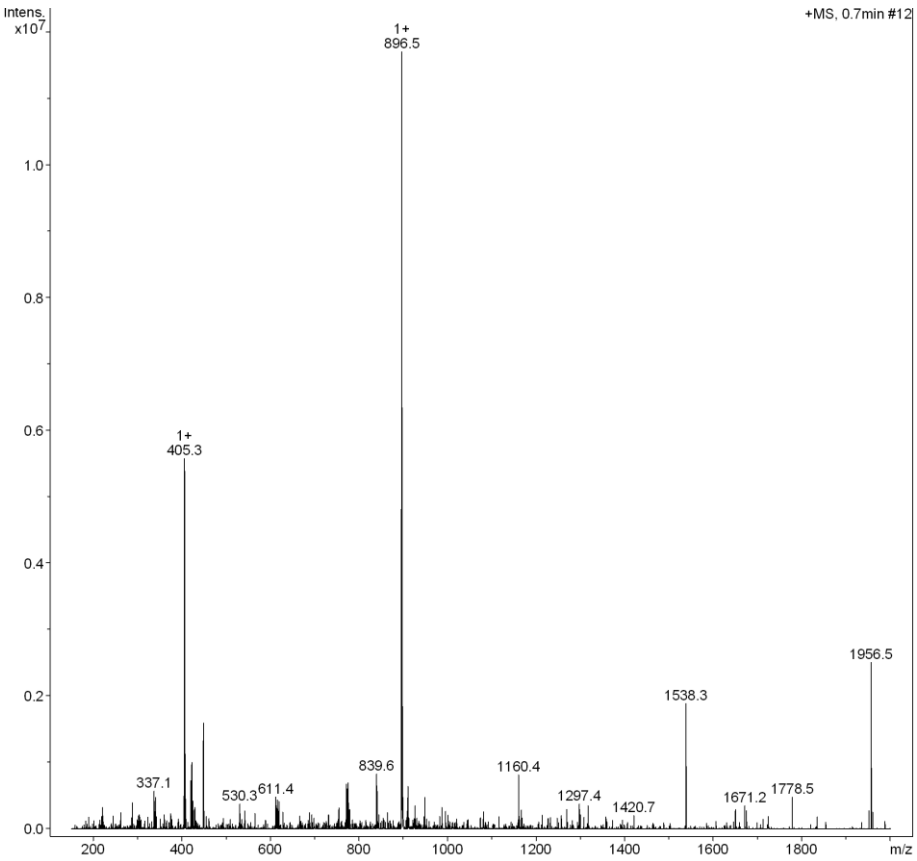


Figure S5. ESI-MS spectrum of **2**.

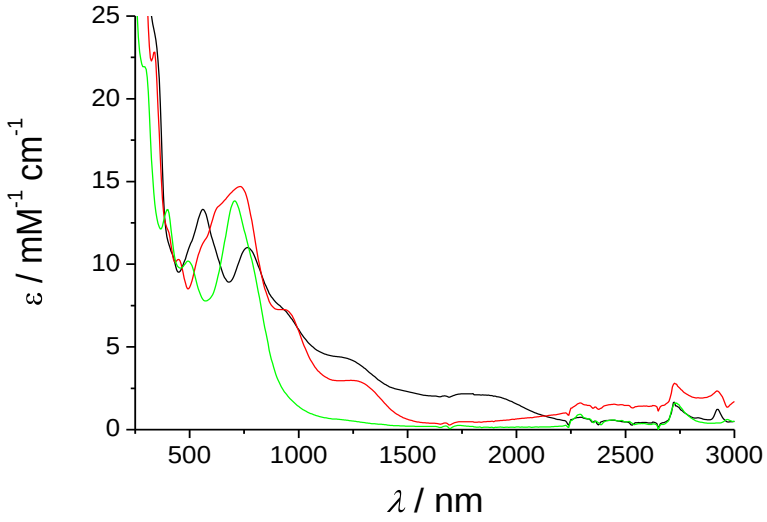


Figure S6. UV-Vis-NIR spectra of CH_2Cl_2 solutions of : **2** (black), $\mathbf{2}^{+}$ (red) and $\mathbf{2}^{2+}$ (green). *T* = 298 K, *l* = 1.000 cm.

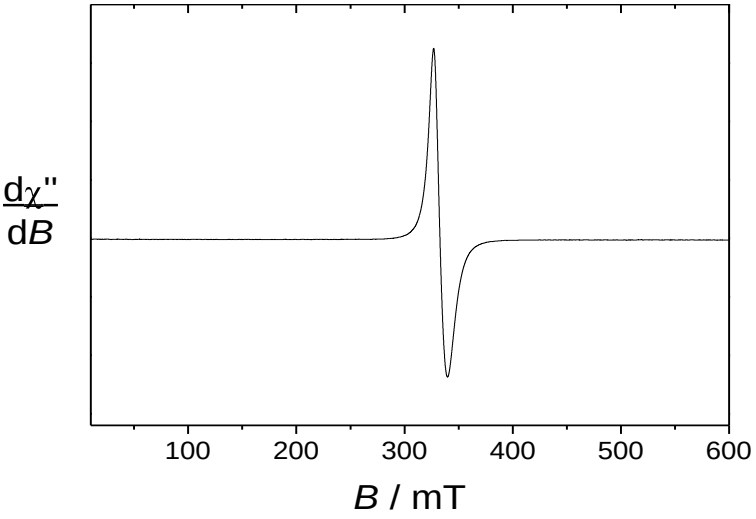


Figure S7. Powder EPR spectrum of **2** at 100 K. Microwave freq. 9.44 GHz, power 0.11 mW, Mod Amp. 0.4 mT, Freq. 100 KHz.

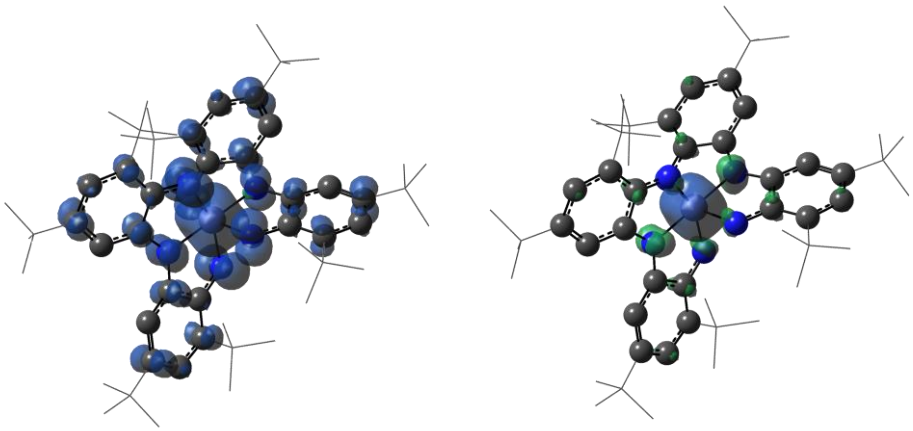


Figure S8. Spin density plots for the sextet (left) and the doublet (right) for Mn complex **2**.

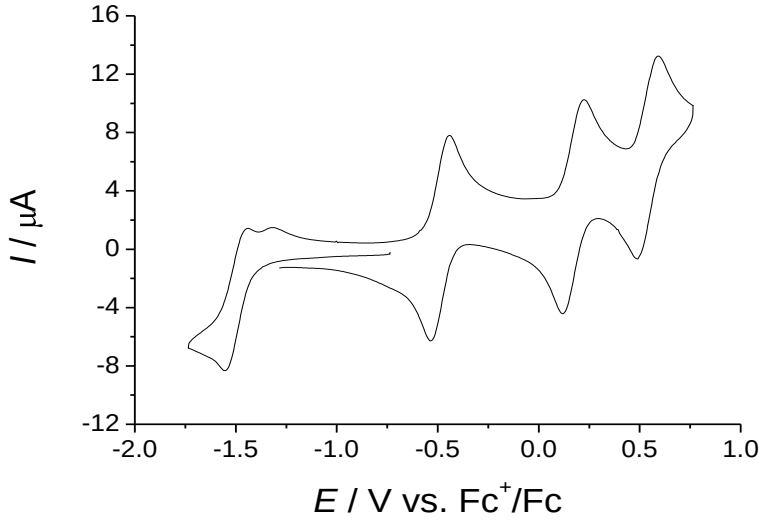


Figure S9. CV curve of a 1 mM CH_2Cl_2 (+0.1 M TBAP) solution of **2**. *T* = 298 K, scan rate = 0.1 V s^{-1}.

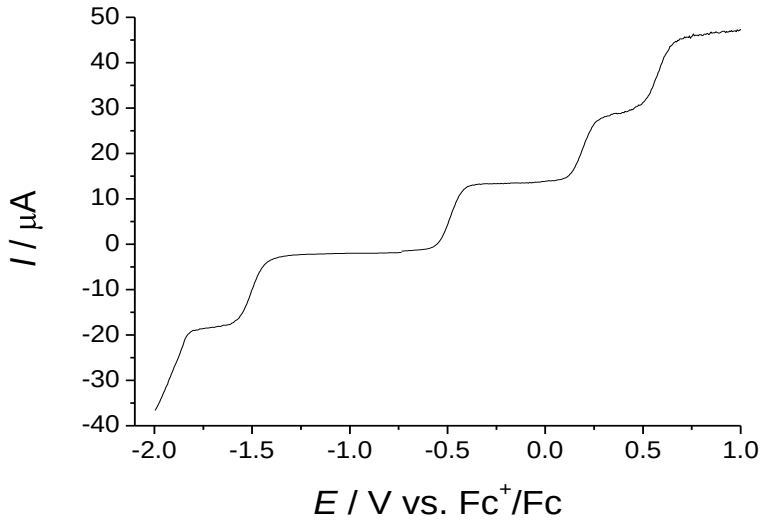


Figure S10. RDE voltammetry curve of a 1 mM CH_2Cl_2 (+0.1 M TBAP) solution of **2**. *T* = 298 K, scan rate = 0.01 V s^{-1}, 500 rpm.

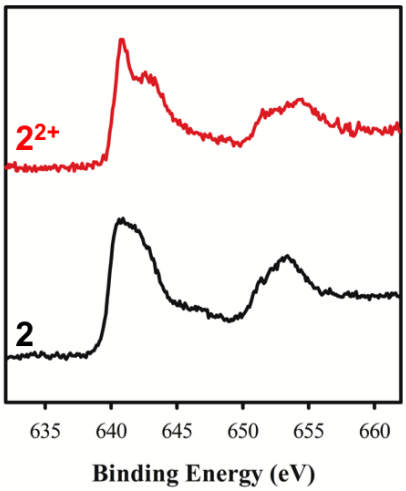


Figure S11. XPS spectra of **2** and $\mathbf{2}^{2+}$ referenced to C 1s (284.8 eV).

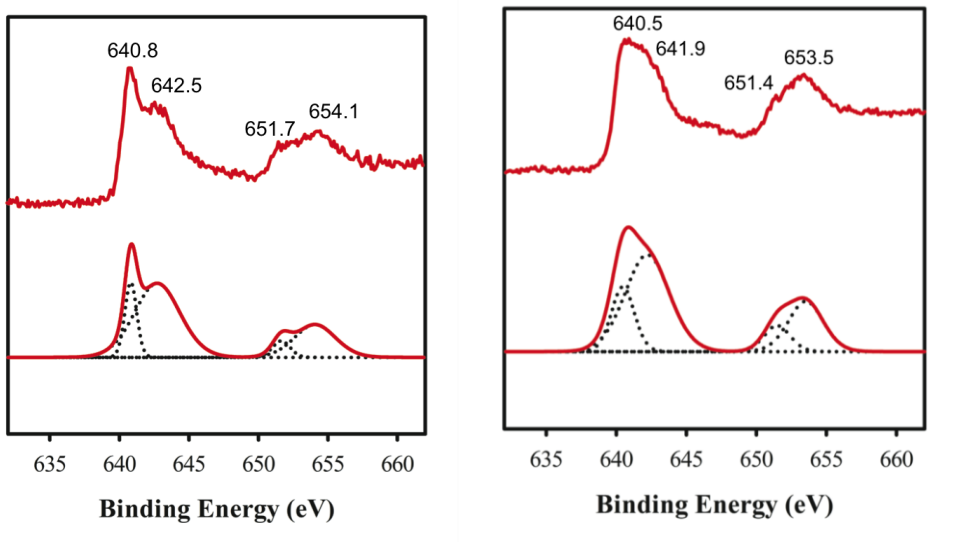


Figure S12. XPS fitted spectra of **2** (right) and $\mathbf{2}^{2+}$ (left).

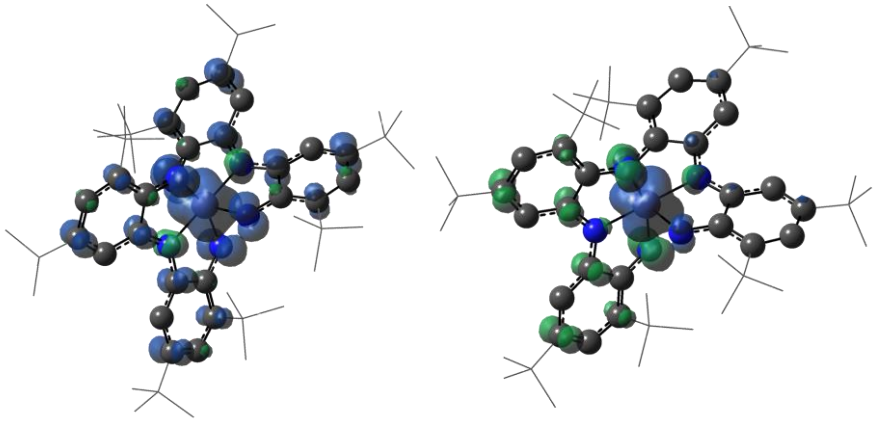


Figure S13. Spin density plots for the quartet (left) and the doublet (right) for Mn complex $\mathbf{[2]}^{2+}$.

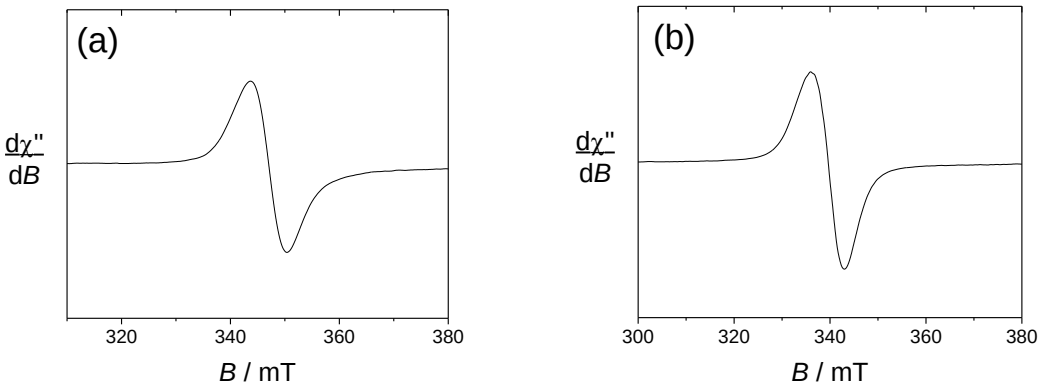


Figure S14. EPR spectrum of a polycrystalline powder of $\mathbf{2}^{2+}$ $(SbF_6^-)_2$ at (a) 6 K and (b) 100 K. Microwave freq. (a) 9.63 GHz, (b) 9.44 GHz, power (a) 5 mW, (b) 0.11 mW, Mod Amp. 0.4 mT, Freq. 100 KHz.

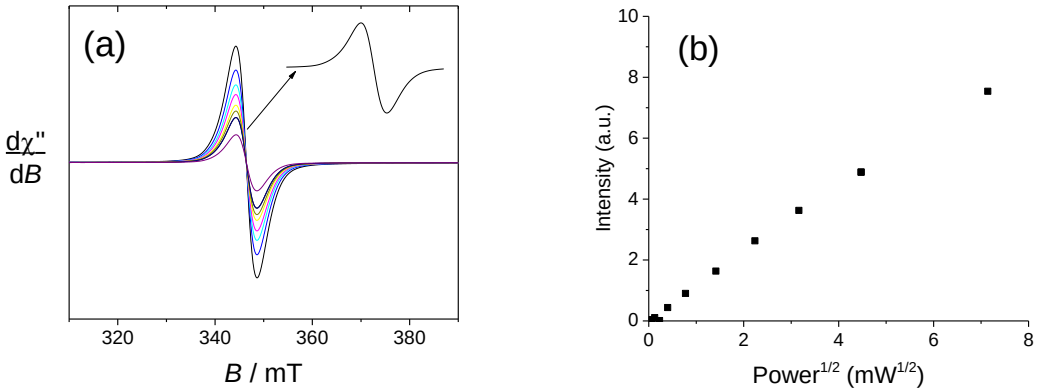


Figure S15. EPR spectra of a polycrystalline powder of $\mathbf{2}^{2+}$ $(SbF_6^-)_2$ dissolved in CH_2Cl_2 (0.5 mM) (a) Spectral evolution upon increasing the temperature (top to bottom T increases from 6 to 30 K) at a constant power of 5 mW and (b) Power saturation curve at 6 K. Microwave freq. 9.63 GHz, Mod Amp. 0.4 mT, Freq. 100 KHz. Insert: zoom at T = 30 K.

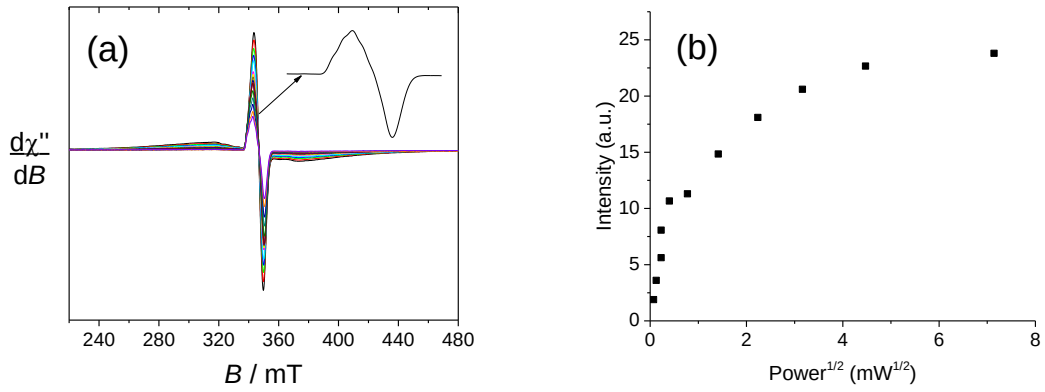


Figure S15. EPR spectra of the electrochemically generated $\mathbf{2}^{2+}$ in CH_2Cl_2 containing 0.1 M TBAP (0.5 mM) (a) Spectral evolution upon increasing the temperature (top to bottom T increases from 6 to 50 K) at a constant power of 5 mW and (b) Power saturation curve at 6 K.

Microwave freq. 9.63 GHz, Mod Amp. 0.4 mT, Freq. 100 KHz. Insert: zoom at T = 30 K. The easy saturation of the (S = ½) signal likely arises from a better spin isolation in the CH_2Cl_2 + TBAP glass.

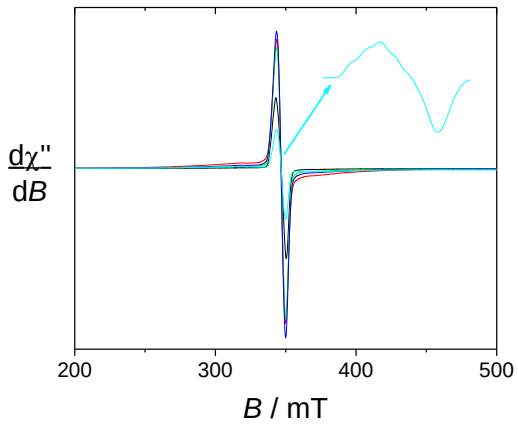


Figure S16. EPR spectra of a polycrystalline powder of $\mathbf{2}^{2+}$ $(SbF_6^-)_2$ dissolved in CH_2Cl_2 (0.5 mM) containing 0.1 M TBAP at various microwave powers: 2, 5, 20, 51, 164 mW. Insert: zoom at 2 mW. The dark blue and red spectra correspond to 51 and 164 mW, respectively. Microwave freq. 9.63 GHz, Mod Amp. 0.4 mT, Freq. 100 KHz, T = 6 K.

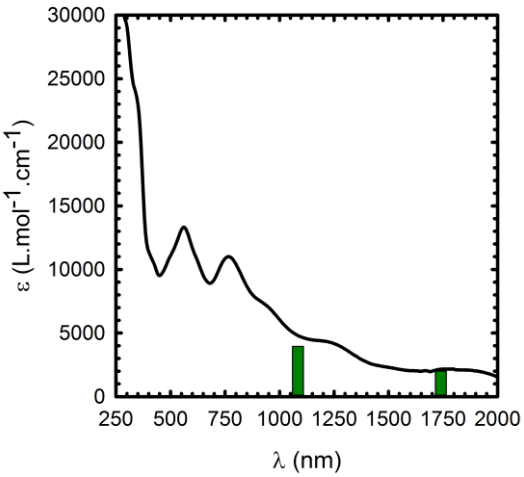
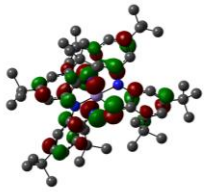
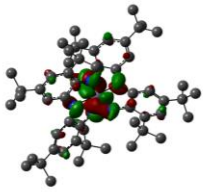
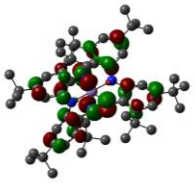
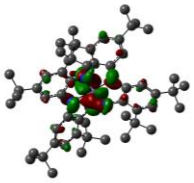


Figure S17. UV-vis-NIR spectrum of **2** with the TD-DFT predicted NIR transitions for the doublet electronic state (f_{osc} > 0.02) plotted as vertical green bars. λ_{calc} = 1084.53 nm, f_{osc} = 0.0481; λ_{calc} = 1739.83 nm, f_{osc} = 0.0243.

Table S1. Natural transition orbitals (NTOs)[20] representing the dominant low energy transitions of doublet **2**.

Excited state properties	Donor	Acceptor
Excited state 3 ν_{calc} = 1739.83 nm f = 0.0243 ν_{exp} = 1800 nm ε = 2170 M^{-1} cm^{-1}		
Excited state 6 ν_{calc} = 1084.53 nm f = 0.0481 ν_{exp} = 1200 nm ε = 4370 M^{-1} cm^{-1}		

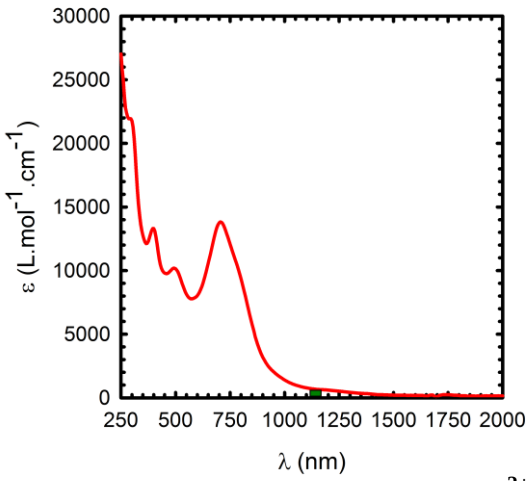
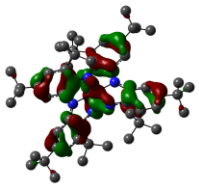
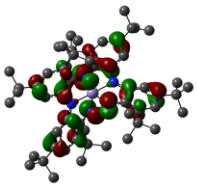


Figure S18. UV-vis-NIR spectrum of $\mathbf{2}^{2+}$ with the TD-DFT predicted NIR transitions for the quartet electronic state (f_{osc} > 0.02) plotted as vertical green bars. λ_{calc} = 1142.31 nm, f_{osc} = 0.0672.

Table S2. NTOs representing the dominant low energy transition for the quartet electronic state of $\mathbf{2}^{2+}$.

Excited state properties	Donor	Acceptor
Excited state 7 ν_{calc} = 1142.31 nm f = 0.0672 ν_{exp} = 1200 nm ε = 900 M^{-1} cm^{-1}		

Computational Details

A) Optimized XYZ coordinates (Å) for $^{2}\mathbf{2}$

Mn	-9E-06	-0.00071	-6.1E-05

N	-1.9411	-0.00021	0.000527
C	4.381742	2.51056	-1.36665
C	3.914889	1.445145	-0.59988
H	4.568452	0.971073	0.129782
C	-1.19394	3.572125	3.361988
C	6.664426	2.275413	-0.22811
H	6.240482	2.363052	0.786033
H	7.68551	2.68946	-0.19569
H	6.752556	1.204179	-0.47326
N	0.357538	1.352251	-1.35335
H	-0.36748	1.832679	-1.88284
C	3.470602	3.136134	-2.26759
H	3.86056	3.942688	-2.89118
C	5.828685	-3.03791	1.270878
C	-1.19801	-3.57324	-3.36108
C	-3.4701	3.13661	2.267587
H	-3.85991	3.943259	2.891149
C	3.915988	-1.44459	0.598578
H	4.569202	-0.96994	-0.13102
C	-5.82616	3.040046	1.273032
C	6.666086	-2.27301	0.226453
H	6.242149	-2.36062	-0.78769
H	7.687415	-2.68644	0.193867
H	6.753596	-1.20179	0.471903
C	-3.91617	-1.44426	-0.59838
H	-4.56927	-0.96962	0.131335
C	-1.97739	-4.59044	-4.2252
H	-2.43468	-5.38982	-3.6196
H	-1.28284	-5.07354	-4.93182
H	-2.77043	-4.10825	-4.8199
C	-5.82903	-3.03745	-1.27051
C	4.383583	-2.50989	1.365042
C	-2.11894	2.817019	2.380512
C	2.121565	-2.81774	2.37916
N	0.358639	-1.35429	1.352347
H	-0.36603	-1.8358	1.881331
C	6.524607	-2.88975	2.648498
H	7.55973	-3.2693	2.600008
H	6.001207	-3.45243	3.437951
H	6.563743	-1.83242	2.958741
C	1.976575	-4.59082	4.225016
H	2.433896	-5.39021	3.619455
H	1.281911	-5.0739	4.931541
H	2.769569	-4.10869	4.819832
N	-0.35893	-1.35401	-1.35272
H	0.365654	-1.83564	-1.88171
C	-2.12205	-2.81741	-2.37926
C	-4.38392	-2.5095	-1.36483
C	-4.38141	2.511001	1.366844

C	1.197357	-3.57355	3.360832
C	-2.56795	-1.02408	-0.69853
C	1.973035	4.589428	-4.22669
H	2.766253	4.1078	-4.82161
H	2.429933	5.389127	-3.62121
H	1.277956	5.072063	-4.93312
C	-0.11674	4.381641	2.590578
H	0.528356	3.7641	1.948392
H	0.538336	4.912756	3.30171
H	-0.59425	5.134296	1.942273
N	-0.35731	1.352307	1.353201
H	0.367832	1.832928	1.882351
C	2.566962	1.023969	-0.69971
C	-1.63052	-1.7634	-1.51977
C	3.472927	-3.13631	2.265894
H	3.863497	-3.94275	2.889258
C	-2.56683	1.024212	0.699801
C	1.630194	-1.76369	1.519622
C	-1.97218	4.590042	4.226274
H	-2.42908	5.3897	3.620734
H	-1.27699	5.072712	4.93257
H	-2.76538	4.108557	4.821333
C	1.194617	3.571686	-3.36236
N	1.941081	-0.00041	-0.00051
C	0.530539	2.574337	-4.34974
H	-0.13719	3.113796	-5.04231
H	-0.06646	1.794702	-3.85448
H	1.299287	2.062235	-4.95169
C	2.119432	2.81663	-2.38067
C	-1.62852	1.762709	1.520756
C	-3.47341	-3.13594	-2.26582
H	-3.86409	-3.94234	-2.88914
C	0.532654	-2.57676	4.348356
H	1.301091	-2.0642	4.950316
H	-0.13467	-3.11674	5.040906
H	-0.06489	-1.79748	3.853199
C	-0.52983	2.574852	4.349417
H	-1.29854	2.062919	4.951555
H	0.138054	3.114343	5.041814
H	0.067016	1.795083	3.854182
C	-0.53338	-2.57645	-4.34866
H	0.133807	-3.11646	-5.04134
H	0.064299	-1.79724	-3.85356
H	-1.30187	-2.06382	-4.95049
C	-0.12122	-4.38373	-2.59011
H	-0.59916	-5.13589	-1.94155
H	0.524782	-3.76678	-1.94826
H	0.533031	-4.9155	-3.3015
C	0.117383	4.381379	-2.59118

H	0.59488	5.134087	-1.94292
H	-0.52782	3.763966	-1.94898
H	-0.53758	4.912451	-3.30245
C	-6.52512	-2.8892	-2.64804
H	-6.56422	-1.83187	-2.95825
H	-7.56026	-3.26868	-2.59943
H	-6.00186	-3.4519	-3.43758
C	5.826511	3.039518	-1.2727
C	-3.91474	1.445474	0.60012
H	-4.56843	0.971387	-0.12942
C	1.628814	1.762476	-1.52084
C	5.813192	-4.53462	0.86697
H	5.335557	-4.67228	-0.11722
H	5.266357	-5.15404	1.595489
H	6.842983	-4.92654	0.803548
C	2.567771	-1.02435	0.69858
C	-6.66628	-2.27256	-0.22595
H	-6.24223	-2.36024	0.788142
H	-7.68762	-2.68594	-0.19327
H	-6.75376	-1.20133	-0.47134
C	-5.81356	-4.53419	-0.86667
H	-5.26683	-5.15359	-1.59528
H	-6.84336	-4.92607	-0.80316
H	-5.33582	-4.67191	0.117459
C	0.120631	-4.38396	2.589693
H	-0.52525	-3.76696	1.947771
H	-0.53375	-4.91572	3.300986
H	0.598614	-5.13614	1.941178
C	-6.66424	2.275924	0.228587
H	-6.24041	2.36347	-0.78561
H	-7.68531	2.690029	0.196265
H	-6.75241	1.204712	0.473823
C	-6.52194	2.892079	2.650739
H	-6.56182	1.83471	2.960732
H	-7.55679	3.272433	2.602527
H	-5.99796	3.454172	3.440225
C	-5.80971	4.536826	0.86942
H	-5.26234	5.155734	1.597973
H	-6.83925	4.929455	0.806246
H	-5.33215	4.674356	-0.11482
C	5.81011	4.536326	-0.86919
H	5.262856	5.155214	-1.59785
H	6.839663	4.928901	-0.80593
H	5.33244	4.673948	0.114989
C	6.52246	2.891422	-2.65031
H	6.562284	1.834036	-2.96025
H	7.557333	3.271685	-2.60199
H	5.998635	3.453528	-3.4399

B) Optimized XYZ coordinates (Å) for ^{6}**2**

Mn	0.000005	-5E-06	0.000047
N	-1.95631	-7.9E-05	0.000783
C	4.35318	2.59435	-1.28949
C	3.891506	1.49975	-0.54305
H	4.554102	0.998574	0.160955
C	-1.16113	3.676378	3.253907
C	6.640888	2.325479	-0.1626
H	6.220595	2.399543	0.854064
H	7.663777	2.734841	-0.12776
H	6.723833	1.257817	-0.42404
N	0.338981	1.365257	-1.35289
H	-0.36971	1.798223	-1.94334
C	3.446312	3.239324	-2.16812
H	3.827616	4.068455	-2.76596
C	5.801833	-3.11079	1.193337
C	-1.16304	-3.67485	-3.25453
C	-3.44473	3.240994	2.16803
H	-3.82572	4.070457	2.765612
C	3.89082	-1.5004	0.544082
H	4.553738	-0.99892	-0.15939
C	-5.80176	3.110881	1.193384
C	6.639895	-2.3265	0.163533
H	6.219653	-2.39977	-0.85321
H	7.66268	-2.7361	0.128542
H	6.723088	-1.25904	0.425701
C	-3.89154	-1.49967	-0.54304
H	-4.55414	-0.99844	0.16092
C	-1.92239	-4.76218	-4.0483
H	-2.35134	-5.53578	-3.39081
H	-1.22109	-5.26682	-4.73279
H	-2.73455	-4.33891	-4.66142
C	-5.80322	-3.10916	-1.193
C	4.351982	-2.59565	1.289849
C	-2.09229	2.898758	2.294407
C	2.092337	-2.89882	2.294311
N	0.338142	-1.36593	1.352932
H	-0.3713	-1.8014	1.940644
C	6.489409	-2.97714	2.57677
H	7.528321	-3.34608	2.52726
H	5.965906	-3.55615	3.353943
H	6.517368	-1.9243	2.903081
C	1.920333	-4.76386	4.047698
H	2.349348	-5.5375	3.390291
H	1.218864	-5.26845	4.732056
H	2.732393	-4.34062	4.660966
N	-0.33899	-1.36536	-1.35278
H	0.369685	-1.79832	-1.94325
C	-2.09384	-2.89738	-2.29453

C	-4.35323	-2.5943	-1.28943
C	-4.35192	2.595692	1.289895
C	1.161204	-3.67649	3.253785
C	-2.55797	-1.06286	-0.66123
C	1.922283	4.762051	-4.04848
H	2.734423	4.338763	-4.66162
H	2.351243	5.535675	-3.39103
H	1.220952	5.26666	-4.73296
C	-0.04507	4.410624	2.461921
H	0.591339	3.739653	1.866951
H	0.61196	4.959987	3.15725
H	-0.48647	5.140757	1.76423
N	-0.3381	1.365931	1.352912
H	0.371291	1.801065	1.940939
C	2.557951	1.062885	-0.66125
C	-1.61942	-1.80897	-1.48263
C	3.444783	-3.24102	2.167931
H	3.825785	-4.0705	2.765476
C	-2.55729	1.063304	0.662154
C	1.618369	-1.80981	1.482895
C	-1.92018	4.763871	4.047723
H	-2.34905	5.537541	3.390256
H	-1.2187	5.268394	4.732116
H	-2.73235	4.34076	4.660944
C	1.162969	3.674732	-3.25465
N	1.956321	0.000109	0.000792
C	0.54904	2.712835	-4.30804
H	-0.11863	3.269459	-4.987
H	-0.03825	1.891207	-3.87135
H	1.344529	2.253501	-4.91745
C	2.093788	2.89731	-2.29464
C	-1.61833	1.809793	1.482932
C	-3.44637	-3.23934	-2.16802
H	-3.8277	-4.06847	-2.76584
C	0.546717	-2.71479	4.307032
H	1.34186	-2.25606	4.91734
H	-0.12175	-3.27146	4.985161
H	-0.03979	-1.89275	3.870098
C	-0.54682	2.714661	4.307239
H	-1.34205	2.256037	4.917513
H	0.121666	3.271288	4.985385
H	0.039631	1.892531	3.870388
C	-0.54912	-2.71298	-4.30795
H	0.118537	-3.26962	-4.98691
H	0.03818	-1.89136	-3.87127
H	-1.34461	-2.25365	-4.91735
C	-0.04668	-4.40926	-2.46312
H	-0.48785	-5.1398	-1.7657
H	0.589651	-3.7384	-1.86796

H	0.610298	-4.95822	-3.15881
C	0.046626	4.409139	-2.46322
H	0.487811	5.139742	-1.76588
H	-0.58962	3.73828	-1.86796
H	-0.61043	4.958033	-3.15889
C	-6.49082	-2.97533	-2.5764
H	-6.51855	-1.92249	-2.90271
H	-7.52982	-3.34404	-2.52685
H	-5.96752	-3.55448	-3.35361
C	5.803129	3.109302	-1.19302
C	-3.89077	1.500487	0.544068
H	-4.55369	0.999055	-0.15943
C	1.619399	1.808919	-1.48271
C	5.79751	-4.60193	0.76853
H	5.323465	-4.72951	-0.21869
H	5.253914	-5.23541	1.48695
H	6.830784	-4.98394	0.702089
C	2.557328	-1.06326	0.662164
C	-6.64117	-2.32476	-0.16318
H	-6.22098	-2.39812	0.853575
H	-7.66403	-2.7342	-0.12819
H	-6.7242	-1.25727	-0.42532
C	-5.7992	-4.60031	-0.76827
H	-5.2557	-5.23383	-1.48673
H	-6.83253	-4.98217	-0.70184
H	-5.32517	-4.72804	0.218942
C	0.045273	-4.41092	2.461776
H	-0.59121	-3.74007	1.866746
H	-0.61172	-4.96034	3.157098
H	0.486797	-5.14102	1.764135
C	-6.63981	2.326691	0.163493
H	-6.21954	2.400032	-0.85323
H	-7.66259	2.736325	0.128501
H	-6.72305	1.259214	0.425574
C	-6.48938	2.977129	2.576785
H	-6.51737	1.924266	2.903015
H	-7.52829	3.346097	2.527271
H	-5.96589	3.556077	3.354021
C	-5.79739	4.602047	0.768698
H	-5.2538	5.23546	1.487186
H	-6.83065	4.984091	0.702258
H	-5.32331	4.729701	-0.2185
C	5.798939	4.600675	-0.76908
H	5.255489	5.233764	-1.48797
H	6.832235	4.982653	-0.7027
H	5.324753	4.7289	0.217993
C	6.491057	2.974773	-2.57618
H	6.518862	1.921765	-2.90196
H	7.530043	3.343503	-2.52657

H	5.967949	3.553527	-3.35382

C) Optimized XYZ coordinates (Å) for ^{2}**[2]**$^{2+}$

Mn	-0.00283	-7E-06	-4E-06
N	1.971926	-3.2E-05	-1.6E-05
N	-1.93255	0.000012	0.000008
N	0.32045	1.361701	-1.34757
H	-0.38518	1.813787	-1.91529
N	-0.33533	-1.3518	-1.36885
H	0.371918	-1.78315	-1.95466
C	-4.30862	-2.53119	-1.3376
C	2.543136	1.033056	-0.6762
C	4.326209	2.524552	-1.34984
C	-2.53287	-1.03503	-0.67276
C	1.580032	1.771454	-1.49152
C	-1.58814	-1.76414	-1.51705
C	3.891787	1.463533	-0.59091
H	4.551271	0.989014	0.119212
C	-3.8633	-1.46906	-0.56331
H	-4.52014	-1.00373	0.155287
C	-5.73973	-3.07287	-1.2515
C	-6.58967	-2.32716	-0.20647
H	-6.16952	-2.41467	0.801775
H	-7.59472	-2.75991	-0.18228
H	-6.69737	-1.26422	-0.44935
C	5.756627	3.07516	-1.27934
C	6.620545	2.324277	-0.2498
H	6.21106	2.405109	0.763524
H	7.626458	2.756137	-0.23422
H	6.723573	1.262376	-0.49948
C	-1.13774	-3.56545	-3.37086
C	3.389563	3.150738	-2.24403
H	3.77361	3.953156	-2.85853
C	5.713517	4.57021	-0.87549
H	5.151765	5.178934	-1.59131
H	6.732775	4.970093	-0.8302
H	5.25462	4.696695	0.111506
C	1.118056	3.600493	-3.31368
C	0.033493	4.377894	-2.52216
H	-0.61262	3.743202	-1.90898
H	-0.61172	4.920591	-3.22147
H	0.500407	5.109622	-1.85406
C	6.423284	2.934905	-2.67091
H	6.478643	1.883699	-2.97506
H	7.443571	3.332851	-2.63375
H	5.882207	3.484752	-3.4479
C	-6.42095	-2.91947	-2.63585
H	-6.46947	-1.86693	-2.93574
H	-7.44459	-3.30599	-2.58322

H	-5.89782	-3.47372	-3.4215
C	-1.91621	-4.60409	-4.20627
H	-2.34849	-5.39389	-3.58273
H	-1.22672	-5.08288	-4.90859
H	-2.71742	-4.14249	-4.79322
C	-5.69423	-4.57228	-0.86029
H	-5.14622	-5.17725	-1.58926
H	-6.71525	-4.96542	-0.80445
H	-5.22312	-4.70897	0.119286
C	-0.51398	-2.56244	-4.37704
H	-1.29866	-2.06057	-4.95325
H	0.128531	-3.10267	-5.07997
H	0.09796	-1.7839	-3.91182
C	0.473885	2.61964	-4.32839
H	1.248179	2.13187	-4.93048
H	-0.18397	3.172275	-5.00772
H	-0.12539	1.829271	-3.8669
C	1.887953	4.648347	-4.14577
H	2.336703	5.425197	-3.51739
H	1.189737	5.143229	-4.82848
H	2.676381	4.191925	-4.75392
C	-0.03676	-4.34694	-2.60574
H	0.626912	-3.71619	-2.00708
H	0.59002	-4.88655	-3.3235
H	-0.4877	-5.08123	-1.92988
C	2.054073	2.838845	-2.35085
C	-2.06368	-2.82547	-2.38494
C	-3.39509	-3.14784	-2.25556
H	-3.78923	-3.94518	-2.86917
N	0.320438	-1.36171	1.347541
H	-0.38519	-1.81378	1.915257
C	2.54313	-1.03311	0.676167
C	4.326189	-2.52461	1.349834
C	1.580011	-1.77149	1.491483
C	3.891788	-1.46359	0.590908
H	4.551289	-0.98908	-0.1192
C	5.756601	-3.07524	1.279346
C	6.620544	-2.32436	0.249835
H	6.211068	-2.40516	-0.7635
H	7.62645	-2.75623	0.234254
H	6.723589	-1.26246	0.499528
C	3.389523	-3.15079	2.244008
H	3.773554	-3.95322	2.858513
C	5.713484	-4.57029	0.875479
H	5.151713	-5.17901	1.591274
H	6.732737	-4.97018	0.83019
H	5.2546	-4.69675	-0.11153
C	1.118	-3.60051	3.313638
C	0.033458	-4.37794	2.522121

H	-0.61266	-3.74326	1.908922
H	-0.61176	-4.92063	3.221421
H	0.50039	-5.10967	1.854038
C	6.423243	-2.93501	2.670931
H	6.478607	-1.88381	2.975097
H	7.443527	-3.33297	2.633777
H	5.882151	-3.48487	3.447901
C	0.473795	-2.61963	4.328304
H	1.248069	-2.13184	4.930405
H	-0.18408	-3.17225	5.007638
H	-0.12547	-1.82928	3.866775
C	1.887883	-4.64834	4.14578
H	2.336656	-5.4252	3.517427
H	1.189654	-5.14321	4.828488
H	2.676293	-4.1919	4.753942
C	2.054035	-2.83888	2.350813
N	-0.33528	1.351795	1.368834
H	0.371978	1.783121	1.954651
C	-4.30853	2.531284	1.337618
C	-2.53284	1.035068	0.672776
C	-1.58807	1.764172	1.517036
C	-3.86326	1.46912	0.563342
H	-4.52011	1.003803	-0.15524
C	-5.73964	3.072953	1.25156
C	-6.58978	2.326805	0.207003
H	-6.16975	2.413785	-0.80134
H	-7.5948	2.75963	0.182729
H	-6.69754	1.263992	0.450409
C	-1.1376	3.565476	3.370849
C	-6.42059	2.920131	2.636111
H	-6.46909	1.867714	2.936423
H	-7.44422	3.306678	2.583535
H	-5.89727	3.474671	3.421428
C	-1.91601	4.604244	4.206152
H	-2.34818	5.394052	3.582548
H	-1.2265	5.08301	4.908482
H	-2.71729	4.142759	4.793094
C	-5.69422	4.572201	0.859718
H	-5.14613	5.177494	1.58836
H	-6.71525	4.965299	0.803828
H	-5.22323	4.708485	-0.11998
C	-0.51399	2.562469	4.377116
H	-1.29874	2.06071	4.953319
H	0.128536	3.102685	5.08005
H	0.097905	1.783844	3.911984
C	-0.03652	4.346803	2.60572
H	0.627107	3.715952	2.007117
H	0.590294	4.886396	3.323462
H	-0.48736	5.081105	1.929797

C	-2.06358	2.825517	2.384935
C	-3.39498	3.147922	2.255568
H	-3.78909	3.945262	2.869193

D) Optimized XYZ coordinates (Å) for $^{4}[2]^{2+}$

Mn	-2.5E-05	0.000004	-6E-06
N	1.960464	-5E-06	-5E-06
N	-1.96049	0.000002	-3E-06
N	0.32972	1.352787	-1.3621
H	-0.36681	1.786919	-1.95712
N	-0.32973	-1.35276	-1.36212
H	0.366769	-1.78675	-1.95727
C	-4.3247	-2.51477	-1.36023
C	2.543566	1.026363	-0.68082
C	4.324716	2.514691	-1.36024
C	-2.54358	-1.02639	-0.68081
C	1.588378	1.75554	-1.51582
C	-1.58839	-1.75553	-1.51583
C	3.884847	1.461116	-0.58575
H	4.541202	0.998042	0.134939
C	-3.88484	-1.4612	-0.58573
H	-4.54121	-0.99817	0.134977
C	-5.75448	-3.06434	-1.28419
C	-6.61029	-2.32652	-0.23846
H	-6.19277	-2.41855	0.770561
H	-7.61491	-2.76088	-0.21977
H	-6.71835	-1.26218	-0.47517
C	5.754508	3.064239	-1.28422
C	6.610277	2.326569	-0.23835
H	6.192727	2.418785	0.770645
H	7.61491	2.760907	-0.21971
H	6.718323	1.26219	-0.47487
C	-1.13851	-3.55025	-3.37631
C	3.400267	3.125669	-2.275
H	3.790344	3.91905	-2.89681
C	5.706178	4.564641	-0.8996
H	5.152005	5.16411	-1.62873
H	6.725339	4.963788	-0.84967
H	5.23815	4.703688	0.081274
C	1.138511	3.550313	-3.37625
C	0.046506	4.342008	-2.60926
H	-0.61259	3.718239	-1.99857
H	-0.58533	4.878268	-3.32536
H	0.506499	5.080333	-1.94379
C	6.431851	2.906847	-2.66925
H	6.486535	1.852537	-2.96217
H	7.452991	3.301447	-2.62547
H	5.900603	3.451245	-3.45662
C	-6.43179	-2.90716	-2.66926

H	-6.48649	-1.85289	-2.96233
H	-7.45292	-3.30177	-2.62544
H	-5.90052	-3.45166	-3.45654
C	-1.91662	-4.58173	-4.22116
H	-2.35749	-5.37177	-3.60386
H	-1.22503	-5.0617	-4.92083
H	-2.71155	-4.11391	-4.81184
C	-5.70614	-4.56468	-0.89935
H	-5.15189	-5.16424	-1.62835
H	-6.72529	-4.96385	-0.84944
H	-5.23818	-4.70358	0.081582
C	-0.50389	-2.54838	-4.37659
H	-1.28333	-2.04384	-4.95775
H	0.142648	-3.08872	-5.07601
H	0.10585	-1.77172	-3.90562
C	0.503853	2.548446	-4.3765
H	1.283265	2.043911	-4.9577
H	-0.14273	3.088772	-5.07589
H	-0.10586	1.771784	-3.90548
C	1.916612	4.581786	-4.22112
H	2.357503	5.37182	-3.60383
H	1.225011	5.061762	-4.92077
H	2.711523	4.113959	-4.81183
C	-0.04647	-4.34192	-2.60934
H	0.612622	-3.71813	-1.99868
H	0.585366	-4.87818	-3.32544
H	-0.50643	-5.08025	-1.94385
C	2.066441	2.808045	-2.39174
C	-2.06643	-2.80802	-2.39177
C	-3.40024	-3.1257	-2.27503
H	-3.7903	-3.91906	-2.89687
N	0.329703	-1.35277	1.362104
H	-0.36682	-1.78688	1.957143
C	2.543553	-1.02638	0.680815
C	4.324686	-2.51473	1.360239
C	1.588357	-1.75554	1.515824
C	3.884827	-1.46115	0.585746
H	4.541185	-0.99809	-0.13495
C	5.754469	-3.0643	1.284221
C	6.610231	-2.32668	0.238306
H	6.192667	-2.41893	-0.77068
H	7.614859	-2.76103	0.219674
H	6.718291	-1.26229	0.474787
C	3.400232	-3.12568	2.275016
H	3.790302	-3.91906	2.896836
C	5.70611	-4.56471	0.899658
H	5.151936	-5.16414	1.628823
H	6.725263	-4.96388	0.849734
H	5.238067	-4.70379	-0.0812

C	1.138476	-3.55029	3.376275
C	0.046454	-4.34196	2.609292
H	-0.61265	-3.71817	1.998624
H	-0.58538	-4.87823	3.325388
H	0.506428	-5.08028	1.943797
C	6.431838	-2.90686	2.669236
H	6.486542	-1.85254	2.962115
H	7.452971	-3.30148	2.625448
H	5.900595	-3.45122	3.456636
C	0.503838	-2.54842	4.376535
H	1.283259	-2.04389	4.95773
H	-0.14274	-3.08874	5.075927
H	-0.10587	-1.77174	3.90553
C	1.916571	-4.58177	4.221137
H	2.357433	-5.37182	3.603852
H	1.224975	-5.06172	4.92081
H	2.711506	-4.11395	4.811821
C	2.066409	-2.80804	2.391754
N	-0.32973	1.352771	1.362101
H	0.366774	1.786774	1.957244
C	-4.32469	2.514769	1.360243
C	-2.54359	1.026395	0.680809
C	-1.58838	1.755534	1.515825
C	-3.88485	1.461198	0.585741
H	-4.54121	0.998169	-0.13496
C	-5.75447	3.06436	1.284199
C	-6.6102	2.326779	0.238233
H	-6.19261	2.419046	-0.77073
H	-7.61482	2.761148	0.219569
H	-6.71828	1.262385	0.474697
C	-1.13846	3.550257	3.376283
C	-6.43191	2.906894	2.669175
H	-6.48664	1.852566	2.962022
H	-7.45304	3.301523	2.625339
H	-5.90071	3.451228	3.456624
C	-1.91652	4.58179	4.221125
H	-2.35738	5.371832	3.603825
H	-1.22489	5.061749	4.92076
H	-2.71144	4.114012	4.811852
C	-5.70606	4.564788	0.899686
H	-5.15184	5.164165	1.628857
H	-6.7252	4.963995	0.849805
H	-5.23804	4.703886	-0.08118
C	-0.50387	2.548388	4.376577
H	-1.28332	2.04389	4.957756
H	0.142702	3.08872	5.075975
H	0.105842	1.771694	3.905614
C	-0.04641	4.341862	2.609276
H	0.612639	3.718024	1.998604

H	0.585471	4.878104	3.325348
H	-0.50635	5.080201	1.943778
C	-2.06642	2.808027	2.391771
C	-3.40024	3.125699	2.275029
H	-3.79029	3.919083	2.89685

E) TD-DFT excitation energies and oscillator strengths for **2**

Excited State 1: 2.362-A 0.4836 eV 2564.02 nm f=0.0042 <S**2>=1.144
243A -> 246A 0.14747
244A -> 245A 0.98582
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -3664.82798032
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.866-A 0.6136 eV 2020.49 nm f=0.0014 <S**2>=1.803
243A -> 245A 0.79151
244A -> 246A 0.59831
243B -> 244B 0.10426

Excited State 3: 2.953-A 0.7126 eV 1739.83 nm f=0.0243 <S**2>=1.930
243A -> 245A -0.52244
244A -> 246A 0.75896
243B -> 244B -0.39172

Excited State 4: 3.363-A 0.8467 eV 1464.38 nm f=0.0109 <S**2>=2.578
243A -> 246A 0.94254
244A -> 245A -0.11416
242B -> 246B 0.10961
243B -> 245B -0.29202

Excited State 5: 2.998-A 0.9371 eV 1323.10 nm f=0.0000 <S**2>=1.996
239A -> 246A -0.12412
240A -> 245A 0.22588
241A -> 245A 0.31555
242A -> 246A -0.16853
242B -> 244B 0.90533

Excited State 6: 2.591-A 1.1432 eV 1084.53 nm f=0.0481 <S**2>=1.428
243A -> 245A -0.31247
244A -> 246A 0.25911
243B -> 244B 0.91470

Excited State 7: 3.199-A 1.1776 eV 1052.84 nm f=0.0212 <S**2>=2.309
239A -> 245A 0.17271
240A -> 246A -0.17963
241A -> 246A -0.22227
242A -> 245A 0.30806
241B -> 244B 0.67537
242B -> 245B 0.57773
243B -> 246B 0.11399

Excited State 8: 3.340-A 1.2836 eV 965.90 nm f=0.0000 <S**2>=2.539
239A -> 246A -0.25137
241A -> 245A 0.14447

242A -> 246A -0.45969
241B -> 245B 0.82448
242B -> 244B -0.17246

Excited State 9: 2.862-A 1.3058 eV 949.46 nm f=0.0011 <S**2>=1.798
241B -> 244B -0.65861
242B -> 245B 0.74943

Excited State 10: 2.693-A 1.3776 eV 899.98 nm f=0.0183 <S**2>=1.563
243A -> 246A 0.21426
244A -> 245A -0.12675
242B -> 246B 0.36603
243B -> 245B 0.89288

Excited State 11: 2.259-A 1.4609 eV 848.69 nm f=0.0159 <S**2>=1.025
238A -> 245A 0.15049
243A -> 246A -0.19701
242B -> 246B 0.91186
243B -> 245B -0.31846

Excited State 12: 2.603-A 1.5147 eV 818.56 nm f=0.0136 <S**2>=1.444
242A -> 245A -0.55290
241B -> 244B 0.10596
243B -> 246B 0.81613

Excited State 13: 2.803-A 1.6769 eV 739.37 nm f=0.0000 <S**2>=1.714
240A -> 245A -0.18175
241A -> 245A 0.89108
242A -> 246A 0.32069
244A -> 247A 0.10160
242B -> 244B -0.18537

Excited State 14: 2.819-A 1.6889 eV 734.09 nm f=0.0514 <S**2>=1.737
239A -> 245A -0.18518
240A -> 246A 0.13278
241A -> 246A 0.41545
242A -> 245A 0.72277
241B -> 244B -0.10835
243B -> 246B 0.47885

Excited State 15: 2.371-A 1.7081 eV 725.84 nm f=0.0114 <S**2>=1.156
238A -> 246A -0.18236
241B -> 246B 0.97429

Excited State 16: 3.096-A 1.8529 eV 669.14 nm f=0.0000 <S**2>=2.146
239A -> 246A -0.18892
240A -> 245A 0.67689
242A -> 246A 0.58322
238B -> 245B -0.14686
239B -> 244B 0.29085
241B -> 245B 0.18933

Excited State 17: 3.168-A 1.8824 eV 658.65 nm f=0.0055 <S**2>=2.259
239A -> 245A 0.46417
240A -> 246A -0.22399

241A -> 246A 0.76846
242A -> 245A -0.10705
238B -> 244B -0.21125
239B -> 245B 0.16725
243B -> 246B -0.20019

Excited State 18: 3.206-A 2.0108 eV 616.60 nm f=0.0074 <S**2>=2.319
238A -> 245A 0.33490
240B -> 244B 0.93096

Excited State 19: 2.850-A 2.0110 eV 616.52 nm f=0.0000 <S**2>=1.780
239A -> 246A 0.57026
240A -> 245A 0.58122
241A -> 245A 0.13668
242A -> 246A -0.41348
244A -> 247A 0.16490
240B -> 246B 0.22315
241B -> 245B -0.17992
242B -> 244B -0.17661

Excited State 20: 2.925-A 2.0411 eV 607.43 nm f=0.0435 <S**2>=1.890
239A -> 245A 0.74982
240A -> 246A 0.57501
241A -> 246A -0.23410
242A -> 245A 0.11543
241B -> 244B -0.10279
242B -> 245B -0.10029
243B -> 246B 0.12004

Excited State 21: 2.711-A 2.1525 eV 575.99 nm f=0.1228 <S**2>=1.588
239A -> 245A -0.17632
240A -> 246A 0.58550
241A -> 246A 0.33771
242A -> 245A -0.21653
244A -> 248A 0.16408
238B -> 244B 0.53472
239B -> 245B -0.15278
241B -> 244B 0.22929
242B -> 245B 0.23866
243B -> 246B -0.14178

Excited State 22: 2.610-A 2.2312 eV 555.69 nm f=0.0000 <S**2>=1.453
239A -> 246A -0.39929
241A -> 245A 0.14993
242A -> 246A -0.26257
238B -> 245B -0.11028
239B -> 244B 0.65308
240B -> 246B 0.41473
241B -> 245B -0.31372
242B -> 244B -0.13793

Excited State 23: 3.380-A 2.2496 eV 551.15 nm f=0.0094 <S**2>=2.606
238A -> 246A -0.40264
240B -> 245B 0.89839
241B -> 246B -0.13979

Excited State 24: 2.571-A 2.2665 eV 547.03 nm f=0.0039 <S**2>=1.403
244A -> 248A 0.97863
238B -> 244B -0.15897

Excited State 25: 2.925-A 2.3110 eV 536.49 nm f=0.0000 <S**2>=1.890
239A -> 246A 0.41812
240A -> 245A -0.10953
244A -> 247A -0.26552
238B -> 245B 0.37293
239B -> 244B 0.62235
240B -> 246B -0.41993
241B -> 245B 0.17505

Excited State 26: 2.566-A 2.3544 eV 526.60 nm f=0.0000 <S**2>=1.397
240A -> 245A -0.19445
244A -> 247A 0.92369
239B -> 244B 0.24539
240B -> 246B -0.14325
242B -> 244B 0.10559

Excited State 27: 2.899-A 2.3610 eV 525.13 nm f=0.1035 <S**2>=1.851
239A -> 245A 0.22691
240A -> 246A -0.33860
243A -> 247A 0.10689
238B -> 244B 0.75139
239B -> 245B 0.45596
241B -> 244B -0.10722
242B -> 245B -0.11369

Excited State 28: 2.515-A 2.3675 eV 523.69 nm f=0.0521 <S**2>=1.331
238A -> 245A 0.90827
239B -> 246B -0.14062
240B -> 244B -0.31821
242B -> 247B 0.11296

Excited State 29: 3.242-A 2.4819 eV 499.56 nm f=0.0073 <S**2>=2.378
243A -> 247A 0.98749

Excited State 30: 2.858-A 2.5461 eV 486.95 nm f=0.0159 <S**2>=1.792
237A -> 245A 0.75640
238A -> 246A 0.57376
240B -> 245B 0.23849

F) TD-DFT excitation energies and oscillator strengths for $\mathbf{2}^{2+}$

Excited State 1: 4.083-A 0.3802 eV 3261.26 nm f=0.0008 <S**2>=3.918
243A -> 246A -0.17159
244A -> 245A 0.44117
241B -> 242B 0.88992
244A <- 245A 0.10229
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -3664.46859589
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 4.118-A 0.4737 eV 2617.53 nm f=0.0104 <S**2>=3.990

240B -> 242B -0.14564
241B -> 243B 0.98164
241B -> 244B 0.13962

Excited State 3: 4.208-A 0.6472 eV 1915.74 nm f=0.0038 <S**2>=4.177
243A -> 246A 0.11924
244A -> 245A 0.85950
238B -> 242B -0.10145
240B -> 243B 0.27349
241B -> 242B -0.41663

Excited State 4: 4.047-A 0.7555 eV 1641.14 nm f=0.0071 <S**2>=3.845
243A -> 245A 0.93723
244A -> 246A 0.28033
239B -> 242B -0.17011
241B -> 246B -0.10761

Excited State 5: 4.128-A 0.9227 eV 1343.73 nm f=0.0126 <S**2>=4.011
243A -> 245A -0.20556
244A -> 246A 0.90682
239B -> 242B 0.35864

Excited State 6: 4.090-A 0.9471 eV 1309.09 nm f=0.0000 <S**2>=3.933
243A -> 246A 0.75908
244A -> 245A 0.14756
238B -> 242B 0.10094
240B -> 243B -0.62020

Excited State 7: 4.102-A 1.0854 eV 1142.31 nm f=0.0672 <S**2>=3.957
240B -> 242B 0.84552
241B -> 244B 0.52091

Excited State 8: 4.086-A 1.1352 eV 1092.18 nm f=0.0043 <S**2>=3.924
243A -> 246A 0.39796
244A -> 245A -0.11143
238B -> 242B 0.67774
240B -> 243B 0.58914
240B -> 244B 0.10216
241B -> 242B 0.11131

Excited State 9: 4.560-A 1.2399 eV 999.95 nm f=0.0553 <S**2>=4.949
240A -> 245A 0.11240
241A -> 246A 0.11828
242A -> 245A 0.33975
238B -> 243B 0.59543
240B -> 242B -0.31267
241B -> 243B -0.14685
241B -> 244B 0.61658

Excited State 10: 4.342-A 1.2555 eV 987.50 nm f=0.0000 <S**2>=4.463
241A -> 245A -0.19517
242A -> 246A -0.10532
239B -> 243B 0.97267

Excited State 11: 4.352-A 1.3040 eV 950.79 nm f=0.0516 <S**2>=4.486

240A -> 245A -0.17074
238B -> 243B 0.77445
240B -> 242B 0.31656
241B -> 243B 0.10867
241B -> 244B -0.50412

Excited State 12: 4.076-A 1.3086 eV 947.46 nm f=0.0771 <S**2>=3.903
243A -> 245A 0.22739
244A -> 246A -0.30068
239B -> 242B 0.90302
240B -> 245B -0.13612
241B -> 246B -0.15478

Excited State 13: 4.059-A 1.3736 eV 902.65 nm f=0.0624 <S**2>=3.869
243A -> 246A -0.43583
244A -> 245A 0.19447
238B -> 242B 0.70762
240B -> 243B -0.40554
240B -> 244B -0.28676
241B -> 242B -0.16335

Excited State 14: 4.789-A 1.3863 eV 894.38 nm f=0.0000 <S**2>=5.483
240A -> 246A -0.35330
241A -> 245A -0.11854
242A -> 246A -0.37402
241B -> 245B 0.84620

Excited State 15: 4.039-A 1.5202 eV 815.58 nm f=0.0217 <S**2>=3.829
239A -> 246A -0.14390
243A -> 245A 0.12816
239B -> 242B 0.13361
241B -> 246B 0.96820

Excited State 16: 4.380-A 1.6069 eV 771.59 nm f=0.0405 <S**2>=4.546
240A -> 245A -0.17788
242A -> 245A 0.91048
238B -> 243B -0.17387
238B -> 244B -0.10908
240B -> 242B 0.20379
241B -> 244B -0.18635

Excited State 17: 4.486-A 1.6231 eV 763.89 nm f=0.0000 <S**2>=4.780
241A -> 245A 0.93333
237B -> 242B 0.10380
238B -> 245B 0.13302
239B -> 243B 0.19062
239B -> 244B 0.19727

Excited State 18: 4.541-A 1.8148 eV 683.20 nm f=0.0336 <S**2>=4.904
239A -> 245A 0.28020
243A -> 246A -0.16324
238B -> 242B 0.11952
239B -> 246B 0.11396
240B -> 243B -0.13733
240B -> 244B 0.91507

Excited State 19: 4.296-A 1.8529 eV 669.14 nm f=0.0000 <S**2>=4.363
240A -> 246A -0.21148
241A -> 245A -0.12758
242A -> 246A 0.67166
237B -> 242B 0.58939
239B -> 244B 0.23630
240B -> 246B -0.19681
241B -> 245B 0.17105

Excited State 20: 4.518-A 1.8577 eV 667.41 nm f=0.0043 <S**2>=4.854
240A -> 245A -0.29090
241A -> 246A 0.77078
242A -> 245A -0.12340
236B -> 242B 0.34156
238B -> 244B -0.37903
239B -> 245B -0.18477

Excited State 21: 4.187-A 1.8928 eV 655.04 nm f=0.0000 <S**2>=4.132
240A -> 246A 0.12977
242A -> 246A -0.41158
237B -> 242B 0.78602
239B -> 244B -0.30600
240B -> 246B 0.24961
241B -> 245B -0.14303

Excited State 22: 4.136-A 1.9254 eV 643.93 nm f=0.0025 <S**2>=4.027
241A -> 246A -0.25199
236B -> 242B 0.93073
238B -> 244B 0.22288

Excited State 23: 4.331-A 1.9399 eV 639.13 nm f=0.0008 <S**2>=4.439
238A -> 245A 0.16399
237B -> 243B 0.97973

Excited State 24: 4.323-A 1.9775 eV 626.97 nm f=0.0006 <S**2>=4.421
237A -> 245A 0.11957
239A -> 245A -0.11048
236B -> 243B 0.98062

Excited State 25: 4.489-A 1.9889 eV 623.38 nm f=0.0761 <S**2>=4.789
240A -> 245A 0.75771
241A -> 246A 0.48070
242A -> 245A 0.13869
238B -> 244B 0.34487
240B -> 242B 0.13345
241B -> 244B -0.16772

Excited State 26: 4.179-A 2.0529 eV 603.95 nm f=0.0000 <S**2>=4.116
236A -> 245A 0.11397
240A -> 246A -0.36299
241A -> 245A -0.12227
242A -> 246A -0.15505
244A -> 247A -0.14342
239B -> 244B 0.64032

240B -> 246B 0.58926
241B -> 245B -0.17449

Excited State 27: 4.621-A 2.0835 eV 595.08 nm f=0.0362 <S**2>=5.089
238A -> 245A 0.13404
239A -> 246A -0.27736
238B -> 246B 0.18568
240B -> 245B 0.91895

Excited State 28: 4.419-A 2.1029 eV 589.59 nm f=0.0000 <S**2>=4.631
240A -> 246A 0.41893
241A -> 245A -0.11301
242A -> 246A -0.30793
237B -> 242B 0.11740
238B -> 245B -0.28921
239B -> 244B 0.60532
240B -> 246B -0.48411

Excited State 29: 4.245-A 2.1320 eV 581.55 nm f=0.0769 <S**2>=4.255
240A -> 245A -0.42320
241A -> 246A 0.17331
243A -> 247A -0.12220
238B -> 244B 0.78646
239B -> 245B -0.34970

Excited State 30: 4.159-A 2.1554 eV 575.23 nm f=0.0000 <S**2>=4.074
236A -> 245A 0.18319
244A -> 247A 0.96071
238B -> 245B 0.12466
240B -> 246B 0.11776

III. References

1. W. Rundel, *Chem. Ber.*, 1963, **96**, 636.
2. A. J. Koning, *Rec. Trav. Chim. Pays Bas*, 1976, **95**, 160.
3. N. Leconte, J. Ciccione, G. Gellon, C. Philouze and F. Thomas, *Chem. Commun.*, 2014, **50**.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-340.
5. G. A. Bain and J. F. Berry, *J. Chem. Edu.*, 2008, **85**, 532-536.
6. K. Kambe, *J. Phys. Soc. Jpn* 1950, **5**, 48-51.
7. A. P. Ginsberg, *Inorg. Chem.*, 1972, **11**, 2289-2290.
8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V.Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, 2009.
9. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
10. P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Chem. Phys.*, 1994, **98**, 11623-11627.
11. V. Barone, M. Cossi and J. Tomasi, *J. Chem. Phys.*, 1997, **107**, 3210-3221.
12. V. Barone, M. Cossi and J. Tomasi, *J. Comput. Chem.*, 1998, **14**, 404-417.
13. S. Miertus, E. Scrocco and J. Tomasi, *Chem. Phys.*, 1981, **55**, 117-129.
14. J. Tomasi, B. Mennucci and E. Cances, *J. Mol. Struct.*, 1999, **464**, 211-226.
15. L. Noodlemann, *J. Chem. Phys.*, 1981, **74**, 5737-5743.
16. L. Noodlemann and D. A. Case, *Adv. Inorg. Chem.*, 1992, **38**, 423-470.
17. L. Noodlemann and E. R. Davidson, *Chem. Phys.*, 1986, **109**, 131-143.
18. P. Fuentealba, H. Preuss, H. Stoll and L. Vonszentpaly, *Chem. Phys. Lett.*, 1982, **89**, 418-422.
19. A. Nicklass, M. Dolg, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1995, **102**, 8942-8952.
20. R. L. Martin, *J. Chem. Phys.*, 2003, **118**, 4775-4777.