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Characterization of an oxidized Mn(III)-bis(phenolate)dipyrrin Radical Complex and Oxidation Catalysis Control via Ligand-centered Redox Activity

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Table of content:

II. Figures

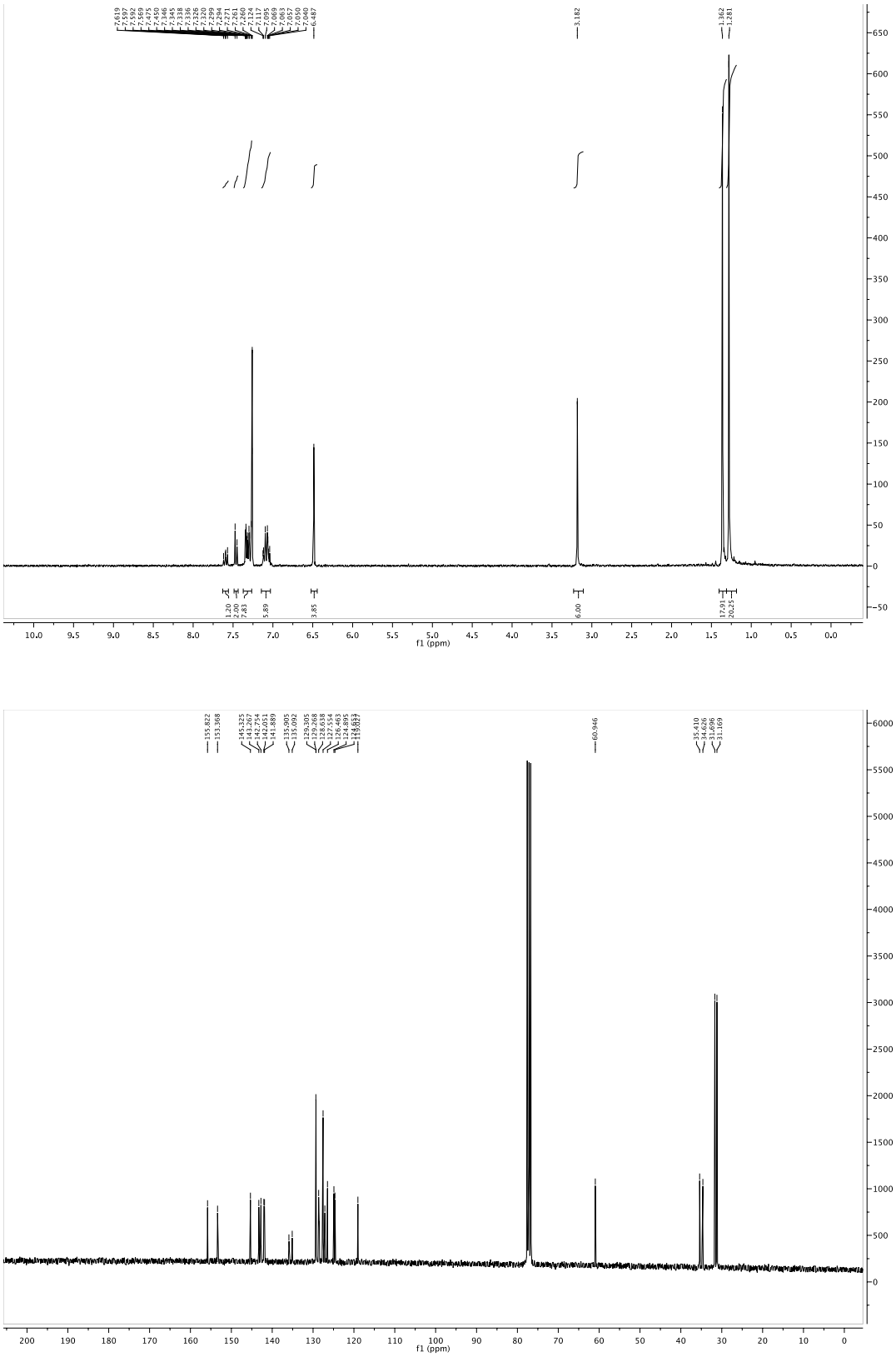

Fig. S1 ^{1}H and ^{13}C NMR spectra of $dppHMe_2$

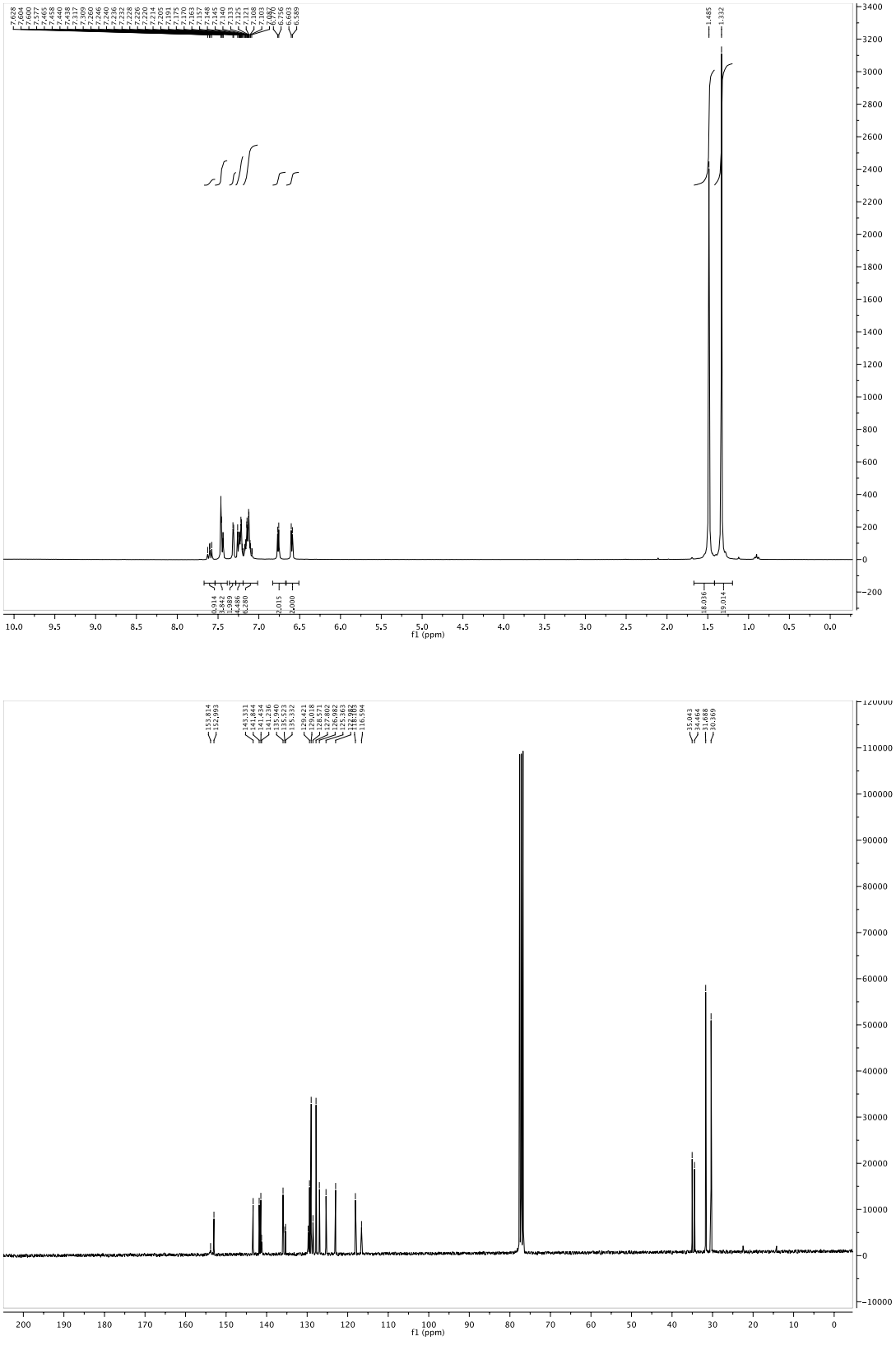

Fig. S2 ^{1}H and ^{13}C NMR spectra of $dppH_3$

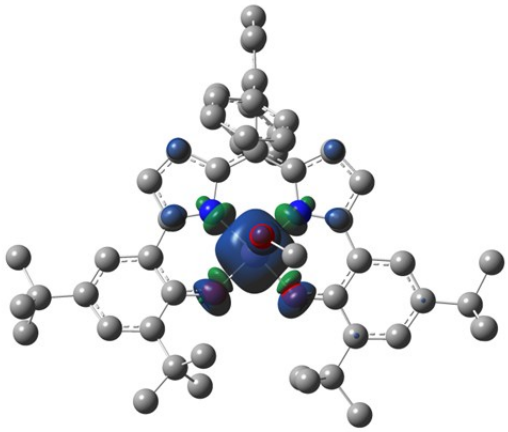

Fig. S3 Spin density plot of **1**. See experimental section for calculation details.

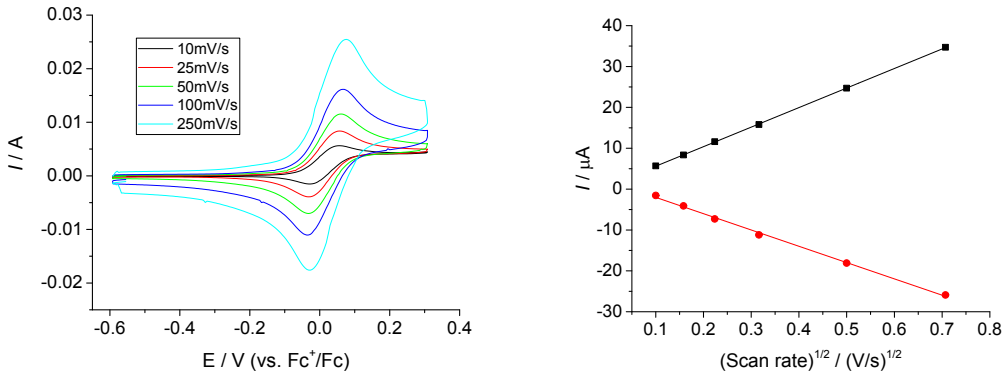

Fig. S4 Cyclic voltammetry curves of **1** in CH_2Cl_2 solution (containing 0.1 M TBAP) at a carbon electrode (left) and plot of I as a function of the square root of the scan rate (right).

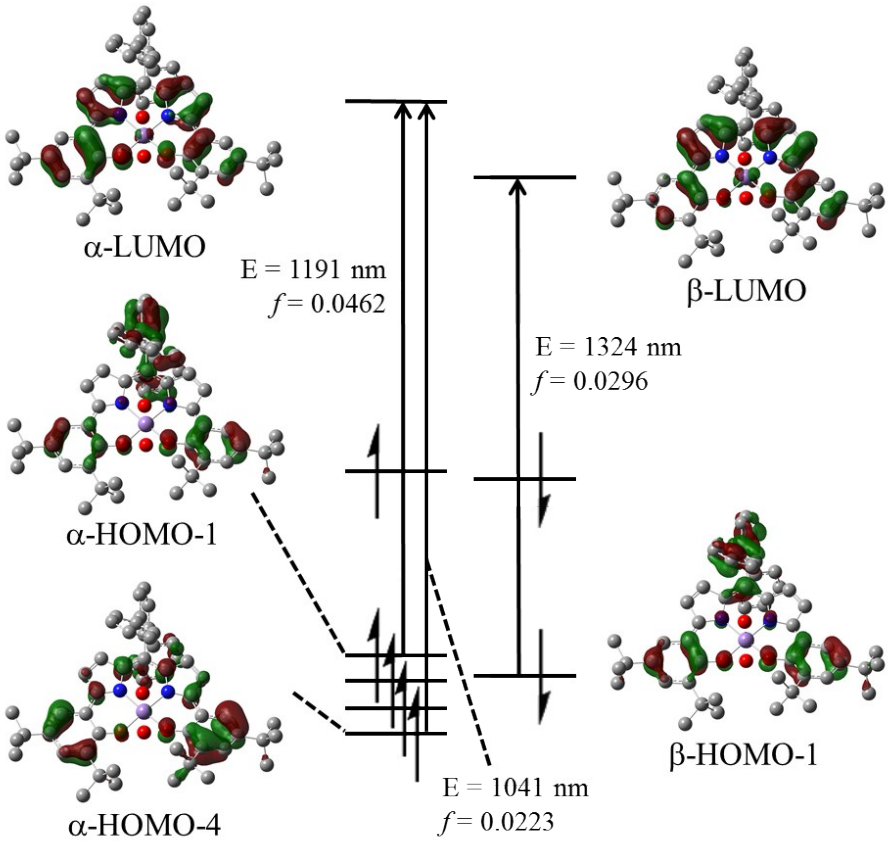

Fig. S5 TD-DFT assignment of the calculated NIR transitions for $\mathbf{1}^{2+}$. As numerous orbitals contribute to each transition (details in tabulated TD-DFT data), only the major components are shown. See experimental section for computational information.

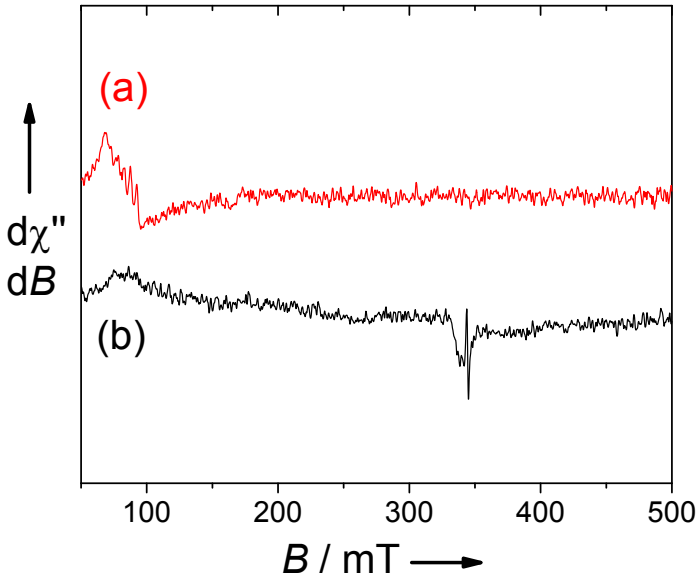

Fig. S6 X-band EPR spectra of an 8 mM CH_2Cl_2 solution of $\mathbf{1}^{2+}$ in (a) parallel and (b) perpendicular modes. Microwave Freq., (a) 9.39 GHz, (b) 9.64 GHz; power, 0.7 mW; Mod. Amp., 1 mT; Mod. Freq., 100 KHz; *T*, 10 K.

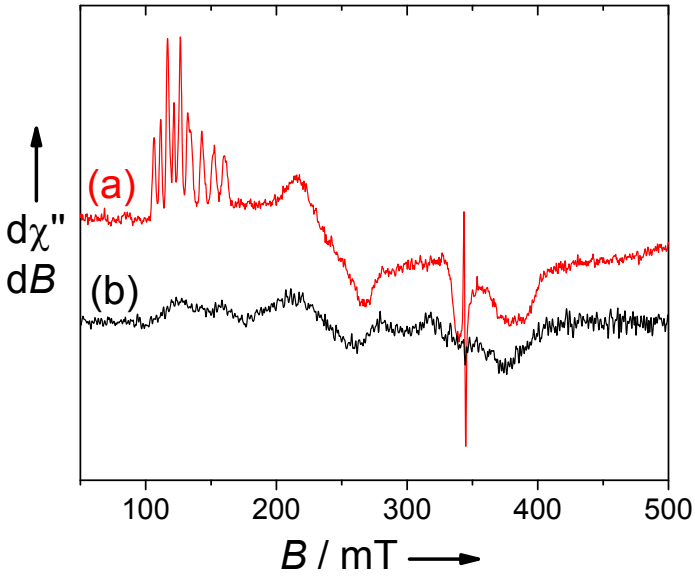

Fig. S7 X-band EPR spectra of an 8 mM CH_2Cl_2 solution of $\mathbf{1}^+$ $\mathbf{SbF_6}^-$ (a) before and (b) after 20 min stirring at room temperature in the presence of one molar equivalent of PhIO. Microwave Freq., 9.64 GHz; power, 4 mW; Mod. Amp., 1 mT; Mod. Freq., 100 KHz; *T*, 10 K.

II. Tables

Table S1. Crystallographic data and structure refinement for **1** and $\mathbf{1}^{+}\ \mathbf{SbF_6^-}$

	1, CH_2Cl_2	[**1**$^+$] • SbF_6^-, 0.47 CH_2Cl_2
Empirical formula	$C_{57}H_{63}Cl_2MnN_2O_3$	$C_{55.47}H_{61.93}Cl_{0.93}F_6MnN_2O_4Sb$
Formula weight	949.93	1144.32
Temperature/K	473.15	200
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_12_12$
a/Å	22.958(5)	11.451(2)
b/Å	11.988(2)	11.555(2)
c/Å	18.415(4)	20.572(4)
α/°	90.00	90.00
β/°	99.50(3)	90.00
γ/°	90.00	90.00
Volume/Å^3	4998.8(17)	2722.0(9)
Z	4	2
ρ_{calc}mg/mm^3	1.262	1.396
m/mm^{-1}	0.417	0.840
F(000)	2008.0	1173.0
Crystal size/mm^3	0.47 × 0.16 × 0.02	0.46 × 0.2 × 0.18
2Θ range for data collection	4.3 to 50°	5 to 50.16°
Index ranges	$-27 \le h \le 27$, $-14 \le k \le 14$, $-21 \le l \le 21$	$-13 \le h \le 13$, $-13 \le k \le 13$, $-24 \le l \le 24$
Reflections collected	36581	23218
Independent reflections	8743[R(int) = 0.0427]	4837[R(int) = 0.0552]
Data/restraints/parameters	8743/79/606	4837/221/343
Goodness-of-fit on F^2	1.055	1.221
Final R indexes [I>=2σ (I)]	$R_1 = 0.0717$, $wR_2 = 0.1838$	$R_1 = 0.0853$, $wR_2 = 0.2120$
Final R indexes [all data]	$R_1 = 0.0989$, $wR_2 = 0.2042$	$R_1 = 0.0901$, $wR_2 = 0.2148$
Largest diff. peak/hole / e Å^{-3}	1.98/-1.31	1.22/-0.84

Table S2. Experimental and calculated coordination sphere bond lengths for **1**.

Bond	X-ray	Calc.
Mn-N(1)	1.956	1.977
Mn-N(2)	1.963	1.984
Mn-O(1)	1.870	1.867
Mn-O(2)	1.857	1.873
Mn-MeOH	2.270	2.294

Table S3. Experimental and calculated coordination sphere bond lengths for $\mathbf{1}^{+}$.

Bond	X-ray	Calc. (S = 5/2)	Calc. (S = 3/2)
Mn-N(1)	1.956	1.977	1.975
Mn-N(2)	1.956	1.981	1.980
Mn-O(1)	1.867	1.895	1.886
Mn-O(2)	1.867	1.904	1.891
Mn-OH_2(1)	2.295	2.314	2.325
Mn- OH_2(2)	2.295	2.333	2.340

III. Computational Details

a) Optimized XYZ coordinates (Å) for **1**

O	-0.94990000	-2.06590000	-0.05410000
N	1.30340000	1.05500000	-0.03600000
O	1.64280000	-1.61030000	-0.25550000
C	-2.57500000	-6.15550000	0.55130000
H	-3.29390000	-6.09830000	1.37720000
H	-1.85480000	-6.94440000	0.79640000
H	-3.11010000	-6.47320000	-0.35110000
N	-1.49100000	0.57630000	-0.20350000
C	-1.54220000	1.97600000	-0.18140000
C	2.67110000	1.05070000	0.03430000
C	2.96160000	-1.41740000	-0.27140000
C	0.88700000	2.38500000	0.05380000
C	-2.77340000	0.12760000	-0.35700000
C	-2.89510000	2.38430000	-0.34090000
H	-3.23490000	3.40980000	-0.36910000
C	-2.25650000	-2.30920000	-0.11800000
C	3.13650000	2.39100000	0.17490000
H	4.16790000	2.70470000	0.23640000
C	3.84860000	-2.51990000	-0.49840000
C	2.44530000	-3.89240000	-2.08260000
H	1.61000000	-3.20060000	-1.96980000
H	2.04340000	-4.88890000	-2.30240000
H	3.04400000	-3.57340000	-2.94470000
C	5.21760000	-2.27750000	-0.43240000
H	5.88940000	-3.11140000	-0.59140000
C	2.03230000	3.21290000	0.18870000
H	2.01580000	4.29150000	0.26830000
C	-4.56210000	-1.55630000	-0.49690000
H	-5.24260000	-0.73920000	-0.69280000
C	-4.11530000	-3.85820000	-0.12590000
H	-4.48630000	-4.87030000	-0.02670000
C	5.79270000	-1.01740000	-0.17210000
C	7.88410000	-1.78240000	1.01170000
H	7.63880000	-2.83570000	0.83950000
H	7.47510000	-1.50070000	1.98890000
H	8.97700000	-1.69950000	1.06320000
C	3.51430000	-0.12560000	-0.06720000
C	-6.53920000	-3.20170000	-0.58710000
C	7.32320000	-0.87000000	-0.10510000
C	2.51960000	-4.46170000	0.40280000
H	3.15990000	-4.50700000	1.29280000
H	2.14970000	-5.47490000	0.20500000
H	1.66490000	-3.82130000	0.61880000
C	-0.71680000	4.28450000	0.17110000
C	3.32220000	-3.93480000	-0.80810000
C	-2.74920000	-3.64710000	0.03180000
C	4.91710000	0.03940000	-0.00490000
H	5.30780000	1.03160000	0.17470000
C	-3.18780000	-1.25950000	-0.34060000
C	-0.93660000	4.76110000	1.48590000
C	-0.83260000	5.16810000	-0.92730000
C	-1.81220000	-4.82940000	0.34590000
C	-3.65420000	1.24880000	-0.46260000
H	-4.72460000	1.20620000	-0.59580000
C	-6.69600000	-4.18920000	-1.76810000
H	-6.34360000	-3.73870000	-2.70300000
H	-7.74930000	-4.46760000	-1.89920000
H	-6.12590000	-5.11030000	-1.60710000
C	4.45740000	-4.94570000	-1.07480000
H	5.08100000	-4.65580000	-1.92850000
H	4.01610000	-5.92140000	-1.30780000
H	5.10740000	-5.08170000	-0.20260000
C	7.75830000	0.57610000	0.19810000
H	8.85200000	0.63280000	0.24180000
H	7.37090000	0.92480000	1.16250000
H	7.42350000	1.27380000	-0.57830000
C	-5.05330000	-2.84460000	-0.40870000
C	-1.12360000	6.52060000	-0.67940000
H	-1.19630000	7.20020000	-1.52360000

b) Optimized XYZ coordinates (Å) for $\mathbf{1}^{+}$

Mn(Fragment=1)	-0.04436332	0.56085265	0.01367646
C(Fragment=2)	0.12909428	-2.84566297	-0.06794609
O(Fragment=2)	-1.42814832	1.82197414	0.23941422
C(Fragment=2)	0.25554157	-7.09543478	-0.76663055
H(Fragment=2)	0.27703609	-8.16588119	-0.94924008
N(Fragment=2)	-1.38771014	-0.88539481	0.08827557
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H(Fragment=2)	2.69486736	-5.80557047	2.22377420
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C(Fragment=2)	7.10559863	3.51384418	1.37378513
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H	-8.45270000	-2.26260000	-1.00460000
C	-0.44410000	2.81730000	-0.01540000
C	-7.07530000	-3.86300000	0.70520000
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H	-6.98730000	-3.18100000	1.55870000
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H	9.03810000	-1.19420000	-1.42510000
H	7.57750000	-0.64070000	-2.26970000
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H	-1.52430000	8.04750000	0.78360000
C	-1.22880000	6.11590000	1.69070000
H	-1.39190000	6.47230000	2.70400000
C	-1.03710000	-4.55040000	1.65570000
H	-1.73240000	-4.46970000	2.50030000
H	-0.46950000	-3.62190000	1.58950000
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H	-0.16550000	-5.87510000	-0.63650000
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H	-1.40350000	-5.27020000	-1.75260000
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C	0.38360000	4.08110000	-2.88600000
C	-1.81660000	5.01000000	-3.21600000
C	0.42750000	3.72090000	-4.23330000
H	1.23560000	3.87050000	-2.24990000
C	-1.77370000	4.64700000	-4.56160000
H	-2.69890000	5.50540000	-2.81910000
C	-0.65000000	3.99850000	-5.07560000
H	1.31190000	3.22530000	-4.62480000
H	-2.62060000	4.86750000	-5.20610000
H	-0.61370000	3.71320000	-6.12350000
C	-0.95770000	3.84410000	2.67220000
C	0.20900000	3.27140000	3.20330000
C	-2.18130000	3.56820000	3.30190000
C	0.14690000	2.43340000	4.32090000
H	1.16910000	3.48720000	2.74680000
C	-2.24580000	2.72790000	4.41460000
H	-3.09190000	4.00500000	2.90160000
C	-1.08190000	2.15350000	4.92670000
H	1.06480000	2.02010000	4.73260000
H	-3.20640000	2.52030000	4.87790000
H	-1.12860000	1.50240000	5.79530000
Mn	0.12640000	-0.54160000	0.00410000
O	0.13710000	-0.42990000	2.29570000
H	-0.00570000	0.48070000	2.61090000
C	1.24810000	-0.99500000	3.00910000
H	2.18150000	-0.47080000	2.77540000
H	1.06050000	-0.96640000	4.08780000
H	1.33050000	-2.03240000	2.68520000

C(Fragment=2)	-2.74709009	-0.71910712	0.16170406
C(Fragment=2)	-7.12542712	1.69484175	0.58285304
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C(Fragment=2)	-7.74148405	0.28909738	0.45729526
H(Fragment=2)	-8.83274586	0.36048163	0.50925512
H(Fragment=2)	-7.41826740	-0.37323437	1.26885368
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C(Fragment=2)	-7.67277695	2.56941340	-0.57165109
H(Fragment=2)	-7.39142975	2.15560172	-1.54655864
H(Fragment=2)	-7.29964703	3.59796702	-0.52312545
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H(Fragment=2)	-7.20117148	3.32027423	2.07658190
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H(Fragment=2)	-1.29436595	3.93092217	-0.88443742
H(Fragment=2)	-1.55817790	5.65734306	-0.57955572
H(Fragment=2)	-2.76253974	4.72592385	-1.48396831
C(Fragment=2)	-2.78909211	4.36008460	0.66942451
C(Fragment=2)	-3.79326059	5.50328866	0.92433892
H(Fragment=2)	-4.50651641	5.62135731	0.10093633
H(Fragment=2)	-3.24349502	6.44607397	1.01316391
H(Fragment=2)	-4.35571050	5.36416071	1.85472485
C(Fragment=2)	-1.80907179	4.34924569	1.86836516
H(Fragment=2)	-2.34597928	4.14375597	2.80228905
H(Fragment=2)	-1.32444949	5.32677677	1.96965618
H(Fragment=2)	-1.02587787	3.59949797	1.73904453
C(Fragment=2)	7.52235106	2.90927977	-1.04411650
H(Fragment=2)	7.09216700	3.85229576	-1.39806154
H(Fragment=2)	7.38869211	2.16121120	-1.83367713
H(Fragment=2)	8.59783450	3.06952028	-0.90734524
O(Fragment=3)	0.16170555	0.77908816	2.33416408
H(Fragment=3)	1.01587562	0.64147856	2.77324804
H(Fragment=3)	-0.18154597	1.62758885	2.65778457
O(Fragment=4)	-0.27976726	0.48121645	-2.29831701
H(Fragment=4)	0.33308158	1.06444421	-2.77289193
H(Fragment=4)	-0.29272091	-0.36317256	-2.78701658
C(Fragment=2)	1.49199804	4.98693175	0.21387639
H(Fragment=2)	0.77301711	4.21264526	0.48153975
H(Fragment=2)	0.93531724	5.88495733	-0.07783619
H(Fragment=2)	2.08740803	5.23537046	1.10051507
C(Fragment=2)	2.40794005	4.52746384	-0.94252585
C(Fragment=2)	3.34274340	5.70445073	-1.29232762
H(Fragment=2)	2.73679994	6.55105908	-1.63147905
H(Fragment=2)	4.03915277	5.45456360	-2.10102880
H(Fragment=2)	3.92248217	6.04926056	-0.42885345
C(Fragment=2)	1.57357206	4.22250023	-2.21079759
H(Fragment=2)	2.22483489	3.90456470	-3.03424555
H(Fragment=2)	1.04404394	5.12509497	-2.53580727
H(Fragment=2)	0.83025394	3.44472051	-2.02737647

c) Optimized XYZ coordinates (Å) for **12**$^{+}$

Mn	-0.05819000	0.55736200	0.02944700
C	0.19282700	-2.84165400	-0.06711600
O	-1.48526700	1.79317800	0.21914500
C	0.42006200	-7.06208300	-0.85586200
H	0.46760000	-8.12712400	-1.06167300
N	-1.36367100	-0.91526600	0.09872400
C	0.73450000	-6.58447900	0.41320300
H	1.00943100	-7.27909000	1.20081800
O	1.18985700	1.96740900	-0.23412400
C	-0.37316700	-3.87964900	-2.74297500
C	2.22098200	-5.16886300	2.67722800
H	2.91776600	-5.76851800	2.09714200
C	2.78450700	-0.37403400	0.15829700
C	0.28802100	-4.31799700	-0.31542600
C	3.57195300	-1.60135300	0.17471400
H	4.64937800	-1.65669100	0.21174600
C	4.48527700	3.39328100	-0.36697000
H	4.97340200	4.33513700	-0.57756900

C	0.66724400	-5.21442300	0.71255000
C	5.33226400	2.31579800	0.06210900
C	6.83188600	2.57123300	0.24227600
C	7.03066600	3.68543500	1.30161800
H	6.55953700	4.62988800	1.00921100
H	8.10003500	3.88169500	1.43166000
H	6.62124100	3.38726500	2.27308900
C	3.32437400	0.92395100	0.10437500
C	4.73330600	1.10137300	0.26570900
H	5.33015100	0.25212900	0.56570700
C	2.54447400	-4.80857400	3.98543500
H	3.48944100	-5.12966100	4.41387800
C	2.48258500	2.07880700	-0.21342100
C	2.71184300	-2.64091000	0.07097500
H	2.94286600	-3.69407700	0.02144800
C	7.58118100	1.31138500	0.71318700
H	7.21130800	0.95024500	1.68006000
H	8.64281200	1.54379000	0.83912300
H	7.51375000	0.49569500	-0.01639000
C	1.00325400	-4.77048400	2.09852600
C	1.37193900	-2.08785400	0.03711400
C	-2.32570700	-3.00601700	0.01943100
H	-2.39591600	-4.08282800	-0.02664000
N	1.44825600	-0.71386800	0.09678400
C	-1.08322700	-2.25928900	-0.00012300
C	-0.01402900	-4.79668300	-1.61552800
C	0.04615200	-6.17429300	-1.86227800
H	-0.17746200	-6.54205100	-2.85913500
C	0.11219300	-4.01155700	2.87645400
H	-0.85911200	-3.73874600	2.47431600
C	-1.61676600	-3.99888100	-3.38399700
H	-2.32345900	-4.74926800	-3.03986800
C	-1.05109800	-2.21539600	-4.91979100
H	-1.30500400	-1.58857300	-5.76963900
C	1.65158000	-4.05068400	4.74523000
H	1.89628000	-3.78304700	5.76894900
C	-3.33154500	-2.10792500	0.12940200
H	-4.38641200	-2.32862000	0.18654800
C	-4.87740500	0.38300600	0.36685800
H	-5.37376900	-0.57234800	0.28518700
C	0.53568900	-2.92234200	-3.22529000
H	1.52814700	-2.85534000	-2.78825900
C	0.43227800	-3.65830700	4.18792100
H	-0.28394900	-3.09960500	4.78454400
C	0.20222000	-2.09911400	-4.30650800
H	0.94383000	-1.41197500	-4.70876100
C	-3.45413400	0.42563600	0.29369100
C	3.11466300	3.33352200	-0.52804700
C	-2.77059800	1.71896300	0.36426500
C	-1.95631900	-3.17118600	-4.45625000
H	-2.92278300	-3.28416500	-4.93847900
C	-2.73383200	-0.77943400	0.17411000
C	-7.15725700	1.52577200	0.60845300
C	-3.54575000	2.91228100	0.59332100
C	-7.75219500	0.11347600	0.46111200
H	-8.84353100	0.17078900	0.51032500
H	-7.42683200	-0.55573200	1.26626700
H	-7.49455000	-0.34208700	-0.50216200
C	-7.70783400	2.41403800	-0.53714900
H	-7.42321000	2.01802700	-1.51809500
H	-7.35334100	3.44821600	-0.47221700
H	-8.80140200	2.44039600	-0.48706700
C	-5.62752600	1.51875100	0.53881300
C	-4.91552200	2.75840400	0.66515400
H	-5.51314900	3.64519500	0.82852700
C	-7.60433600	2.10746100	1.97438400
H	-8.69807400	2.11938800	2.02584600
H	-7.26087400	3.13616800	2.12539200
H	-7.23342600	1.49903300	2.80648900
C	-2.18876200	4.68249300	-0.58383700
H	-1.40729400	3.97182600	-0.85767800
H	-1.73109500	5.67269500	-0.48677900
H	-2.91608500	4.73136400	-1.40200300
C	-2.88772300	4.29790900	0.74198200
C	-3.92497800	5.39685700	1.05382600

H	-4.65310400	5.52449600	0.24522300
H	-3.40458100	6.35247600	1.16897500
H	-4.46658000	5.20742200	1.98756100
C	-1.88250800	4.27884100	1.92045800
H	-2.38976300	4.02314500	2.85830700
H	-1.43727100	5.27135200	2.04541000
H	-1.06837900	3.56976700	1.75190600
C	7.43778200	3.02792300	-1.10934100
H	6.98445600	3.95285200	-1.48148800
H	7.31858300	2.25707700	-1.87859600
H	8.50893600	3.21828300	-0.98495000
O	0.07800300	0.76558500	2.33480400
H	0.70078500	0.33198700	2.93969200
H	-0.23239900	1.57139600	2.77861600
O	-0.28527400	0.48406700	-2.24397500
H	0.08758900	1.18873300	-2.79765900
H	-0.30818900	-0.32580400	-2.79217200
C	1.42029500	5.06175600	0.16486800
H	0.71105000	4.29731400	0.48494100
H	0.85171700	5.94251100	-0.15290400
H	2.03246500	5.35334600	1.02577800
C	2.31188000	4.56465400	-0.99603300
C	3.23609500	5.72928800	-1.41006500
H	2.62070900	6.55936700	-1.76994200
H	3.91699000	5.45186700	-2.22290600
H	3.82865100	6.11214800	-0.57196200
C	1.45251800	4.20496800	-2.23347300
H	2.08384600	3.85117600	-3.05733700
H	0.91947800	5.09452900	-2.58467700
H	0.70722200	3.44036100	-2.00261500

d) TD-DFT excitation energies and oscillator strengths for $\mathbf{1}^{+}$

Excited State 1: 4.496-A 0.9410 eV 1317.54 nm f=0.0583 <S**2>=4.804
231A -> 234A -0.10311
232A -> 233A 0.96249
229B -> 230B 0.21522

Excited State 2: 4.501-A 1.1530 eV 1075.36 nm f=0.0263 <S**2>=4.815
231A -> 233A 0.98316

Excited State 3: 4.432-A 1.4444 eV 858.39 nm f=0.0242 <S**2>=4.662
227A -> 233A -0.19730
229A -> 233A -0.38286
230A -> 233A 0.32898
231A -> 234A 0.14424
232A -> 233A -0.11495
229B -> 230B 0.80051

Excited State 4: 4.480-A 1.5938 eV 777.91 nm f=0.0181 <S**2>=4.766
230A -> 233A 0.92027
232A -> 233A 0.10714
229B -> 230B -0.35978

Excited State 5: 4.473-A 1.7493 eV 708.77 nm f=0.0573 <S**2>=4.752
227A -> 233A 0.13035
229A -> 233A 0.87557
230A -> 233A 0.19352
232A -> 233A -0.11426
227B -> 230B -0.11964
229B -> 230B 0.35335
229B -> 233B -0.10774

Excited State 6: 4.875-A 1.9733 eV 628.30 nm f=0.0049 <S**2>=5.690
224A -> 233A -0.10407
227A -> 233A -0.20938
228A -> 233A 0.51618
229A -> 233A 0.11043
232A -> 234A 0.40805
228B -> 230B 0.65888

Excited State 7: 4.705-A 1.9902 eV 622.99 nm f=0.0137 <S**2>=5.283
227A -> 233A -0.29889
228A -> 233A 0.72975

229A -> 233A 0.10377
232A -> 234A -0.29126
228B -> 230B -0.47769

Excited State 8: 4.509-A 2.0638 eV 600.75 nm f=0.0247 <S**2>=4.833
227A -> 233A 0.85779
228A -> 233A 0.41468
229A -> 233A -0.19518
227B -> 230B -0.12963

Excited State 9: 4.828-A 2.1402 eV 579.30 nm f=0.0001 <S**2>=5.578
232A -> 235A 0.97298

Excited State 10: 4.482-A 2.1759 eV 569.81 nm f=0.0004 <S**2>=4.773
220A -> 233A 0.15708
221A -> 234A 0.12092
222A -> 233A -0.10100
224A -> 233A 0.88511
226A -> 233A 0.27455
228B -> 230B 0.15215

Excited State 11: 4.312-A 2.2167 eV 559.32 nm f=0.0013 <S**2>=4.398
219A -> 235A 0.10421
221A -> 233A -0.17956
223A -> 233A 0.65471
223A -> 235A 0.11983
224A -> 233A -0.20371
225A -> 233A 0.24040
226A -> 233A 0.42436
229B -> 231B 0.41887

Excited State 12: 4.130-A 2.2461 eV 552.01 nm f=0.0014 <S**2>=4.014
221A -> 233A 0.15705
223A -> 233A -0.23068
225A -> 233A -0.13951
226A -> 233A -0.26845
227B -> 231B -0.10893
229B -> 231B 0.88108

Excited State 13: 4.620-A 2.2967 eV 539.84 nm f=0.0335 <S**2>=5.086
219A -> 235A -0.39204
221A -> 233A 0.29487
223A -> 233A 0.41509
223A -> 235A -0.39573
224A -> 235A 0.18983
227A -> 233A -0.12705
231A -> 234A -0.23574
231A -> 235A 0.11316
232A -> 234A -0.13295
226B -> 230B 0.13556
227B -> 230B -0.40581

Excited State 14: 4.523-A 2.3176 eV 534.97 nm f=0.0172 <S**2>=4.864
219A -> 235A 0.26572
221A -> 233A 0.45633
223A -> 233A 0.43567
223A -> 235A 0.25998
224A -> 233A 0.12516
224A -> 235A -0.10234
225A -> 233A -0.14912
226A -> 233A -0.42864
227A -> 233A 0.13371
231A -> 235A -0.16881
232A -> 234A -0.18376
227B -> 230B 0.23000
228B -> 230B 0.10793
229B -> 231B -0.10296

Excited State 15: 4.843-A 2.3186 eV 534.74 nm f=0.0062 <S**2>=5.613
219A -> 235A -0.31847
223A -> 235A -0.36295
224A -> 235A 0.16202
227A -> 233A 0.12135
229A -> 233A 0.10143
231A -> 234A 0.40821

231A -> 235A 0.13873
226B -> 230B -0.18306
227B -> 230B 0.62146

Excited State 16: 4.722-A 2.3458 eV 528.54 nm f=0.0006 <S**2>=5.323
208A -> 235A 0.14462
214A -> 235A -0.10201
215A -> 235A -0.15732
223A -> 235A 0.14386
224A -> 235A -0.30259
231A -> 235A 0.87401

Excited State 17: 4.564-A 2.3882 eV 519.15 nm f=0.0403 <S**2>=4.957
220A -> 233A 0.10384
221A -> 233A 0.25202
222A -> 233A -0.12790
224A -> 233A 0.11622
232A -> 234A 0.73770
223B -> 230B -0.10754
225B -> 230B -0.13544
228B -> 230B -0.47603
228B -> 233B 0.11413

Excited State 18: 4.517-A 2.4179 eV 512.77 nm f=0.0109 <S**2>=4.850
221A -> 233A 0.44237
223A -> 233A -0.18434
224A -> 233A -0.15114
225A -> 233A -0.48853
226A -> 233A 0.65304
232A -> 234A -0.12796
228B -> 230B 0.11082

Excited State 19: 4.799-A 2.4878 eV 498.37 nm f=0.0009 <S**2>=5.507
220A -> 233A -0.12502
221A -> 233A -0.15192
222A -> 233A 0.24916
225A -> 233A -0.15588
225B -> 230B -0.21274
226B -> 230B 0.83003
227B -> 230B 0.28350

Excited State 20: 4.580-A 2.5031 eV 495.33 nm f=0.0271 <S**2>=4.994
220A -> 233A 0.21534
221A -> 233A 0.33536
222A -> 233A -0.44538
223A -> 233A -0.18748
224A -> 233A -0.13614
225A -> 233A 0.54250
223B -> 230B 0.14637
225B -> 230B 0.11008
226B -> 230B 0.36140
227B -> 230B 0.14296
228B -> 230B 0.12643
229B -> 232B -0.20059

Excited State 21: 4.529-A 2.5539 eV 485.47 nm f=0.0111 <S**2>=4.877
220A -> 233A -0.26641
221A -> 233A 0.34538
222A -> 233A 0.55316
223A -> 233A -0.14276
225A -> 233A 0.56168
226A -> 233A 0.18281
223B -> 230B -0.11851
225B -> 230B -0.12238
226B -> 230B -0.11962
229B -> 232B 0.20385

Excited State 22: 4.331-A 2.6339 eV 470.73 nm f=0.0003 <S**2>=4.440
222A -> 233A -0.10212
223B -> 230B 0.13016
225B -> 230B 0.43054
226B -> 230B 0.15676
229B -> 232B 0.83393

Excited State 23: 4.502-A 2.6745 eV 463.59 nm f=0.0399 <S**2>=4.818

221A -> 233A 0.15526
231A -> 234A 0.73695
226B -> 230B 0.20919
227B -> 230B -0.45426
229B -> 233B 0.36971

Excited State 24: 4.759-A 2.6838 eV 461.98 nm f=0.0502 <S**2>=5.411
222A -> 233A 0.34695
224A -> 233A 0.13949
229A -> 234A 0.23768
230A -> 234A -0.16338
232A -> 234A 0.19373
225B -> 230B 0.69441
226B -> 230B 0.11791
229B -> 232B -0.39435

Excited State 25: 4.347-A 2.8042 eV 442.14 nm f=0.0069 <S**2>=4.475
219A -> 233A 0.74760
220A -> 233A -0.34303
222A -> 233A -0.21584
229A -> 235A -0.10210
228B -> 231B 0.26125
229B -> 233B 0.28639

Excited State 26: 4.455-A 2.8166 eV 440.19 nm f=0.0370 <S**2>=4.711
219A -> 233A -0.14963
219A -> 235A 0.10420
220A -> 233A 0.44831
222A -> 233A 0.28032
223A -> 235A -0.10045
231A -> 234A -0.20984
228B -> 231B 0.56241
229B -> 233B 0.47144

Excited State 27: 4.459-A 2.8323 eV 437.75 nm f=0.0366 <S**2>=4.721
219A -> 233A -0.16011
219A -> 235A -0.14464
220A -> 233A -0.21919
222A -> 233A -0.12228
223A -> 235A 0.10678
231A -> 234A 0.18412
228B -> 231B 0.75319
229B -> 233B -0.40195

Excited State 28: 4.416-A 2.8438 eV 435.98 nm f=0.0361 <S**2>=4.626
219A -> 233A 0.52666
220A -> 233A 0.53163
222A -> 233A 0.29144
229A -> 235A -0.10879
231A -> 234A 0.16872
223B -> 230B 0.11645
229B -> 233B -0.42230

Excited State 29: 4.708-A 2.8771 eV 430.93 nm f=0.0003 <S**2>=5.292
194A -> 235A 0.10215
205A -> 235A -0.10413
219A -> 233A -0.24848
219A -> 235A 0.10466
221A -> 235A 0.26893
226A -> 235A -0.10378
227A -> 235A -0.24563
229A -> 234A -0.18279
229A -> 235A -0.37418
230A -> 234A 0.38950
230A -> 235A 0.27759
223B -> 230B -0.24925
224B -> 230B 0.35893
225B -> 230B 0.24011

Excited State 30: 4.715-A 2.8819 eV 430.22 nm f=0.0045 <S**2>=5.308
194A -> 235A -0.10790
205A -> 235A 0.10426
219A -> 233A 0.15053
220A -> 233A 0.19529
221A -> 235A -0.27133

226A -> 235A 0.10229
227A -> 235A 0.24466
229A -> 234A -0.19277
229A -> 235A 0.37327
230A -> 234A 0.44482
230A -> 235A -0.27322
223B -> 230B -0.20001
224B -> 230B 0.33487
225B -> 230B 0.22120

e) TD-DFT excitation energies and oscillator strengths for $\mathbf{1}^{2+}$

Excited State 1: 5.666-A 0.2495 eV 4970.15 nm f=0.0019 <S**2>=7.777
230A -> 233A 0.12288
231A -> 233A -0.55616
232A -> 233A 0.51726
221B -> 229B -0.10168
225B -> 229B 0.21220
226B -> 229B -0.17164
227B -> 229B 0.71823
228B -> 229B -0.26132
231A <- 233A -0.27500
232A <- 233A 0.23755
225B <- 229B 0.11315
227B <- 229B 0.34087
228B <- 229B -0.10075

Excited State 2: 5.434-A 0.6454 eV 1920.91 nm f=0.0043 <S**2>=7.131
231A -> 233A -0.13095
227B -> 229B 0.22584
228B -> 229B 0.94625

Excited State 3: 5.565-A 0.7359 eV 1684.84 nm f=0.0099 <S**2>=7.493
228A -> 233A -0.54466
229A -> 233A 0.19600
232A -> 233A -0.37588
224B -> 229B 0.62284
225B -> 229B 0.14902
226B -> 229B -0.22031
228B -> 229B -0.18217

Excited State 4: 5.397-A 0.8210 eV 1510.11 nm f=0.0010 <S**2>=7.031
228A -> 233A -0.20850
229A -> 233A 0.12874
231A -> 233A 0.58640
232A -> 233A 0.71969
224B -> 229B 0.25390

Excited State 5: 5.358-A 0.9365 eV 1323.85 nm f=0.0296 <S**2>=6.926
225A -> 233A 0.10080
230A -> 233A -0.15141
231A -> 233A 0.25386
232A -> 233A -0.20663
225B -> 229B -0.42757
226B -> 229B 0.52094
227B -> 229B 0.61452

Excited State 6: 5.295-A 1.0414 eV 1190.52 nm f=0.0462 <S**2>=6.758
228A -> 233A 0.11120
229A -> 233A -0.18597
230A -> 233A 0.31224
231A -> 233A 0.53811
232A -> 233A -0.24569
221B -> 229B 0.16286
222B -> 229B 0.11399
224B -> 229B -0.24614
224B -> 230B 0.10489
225B -> 229B 0.48862
226B -> 229B -0.18851
227B -> 229B 0.33675

Excited State 7: 5.378-A 1.0639 eV 1165.40 nm f=0.0051 <S**2>=6.981
231A -> 233A -0.11668
224B -> 229B 0.11321

225B -> 229B 0.61539
226B -> 229B 0.74885
227B -> 229B -0.13991

Excited State 8: 5.161-A 1.1470 eV 1080.98 nm f=0.0140 <S**2>=6.409
225A -> 233A -0.12833
229A -> 233A -0.32246
230A -> 233A 0.80693
224B -> 229B 0.26355
225B -> 229B -0.31024
226B -> 229B 0.17549

Excited State 9: 5.080-A 1.1905 eV 1041.48 nm f=0.0223 <S**2>=6.201
228A -> 233A 0.60415
229A -> 233A -0.35271
230A -> 233A -0.31443
224B -> 229B 0.59776
225B -> 229B 0.10561
226B -> 229B -0.12352

Excited State 10: 5.346-A 1.2347 eV 1004.16 nm f=0.0007 <S**2>=6.894
228A -> 233A 0.49091
229A -> 233A 0.79995
230A -> 233A 0.29764
224B -> 229B 0.11644

Excited State 11: 5.575-A 1.4104 eV 879.07 nm f=0.0066 <S**2>=7.521
224A -> 233A 0.12160
225A -> 233A -0.32171
226A -> 233A -0.20565
227A -> 233A -0.15283
229A -> 233A 0.13112
220B -> 229B -0.14281
221B -> 229B 0.31058
222B -> 229B 0.29589
223B -> 229B 0.73915

Excited State 12: 5.460-A 1.4700 eV 843.42 nm f=0.0014 <S**2>=7.203
225A -> 233A 0.30480
226A -> 233A 0.19272
220B -> 229B 0.14494
221B -> 229B -0.34488
222B -> 229B -0.49768
223B -> 229B 0.65369

Excited State 13: 5.325-A 1.5892 eV 780.15 nm f=0.0052 <S**2>=6.840
225A -> 233A 0.14552
227A -> 233A 0.61180
220B -> 229B 0.11856
221B -> 229B -0.31322
222B -> 229B 0.67719
223B -> 229B 0.11894

Excited State 14: 5.430-A 1.5992 eV 775.28 nm f=0.0006 <S**2>=7.121
225A -> 233A -0.25852
226A -> 233A -0.11725
227A -> 233A 0.76147
221B -> 229B 0.37866
222B -> 229B -0.41088

Excited State 15: 5.466-A 1.7257 eV 718.47 nm f=0.0040 <S**2>=7.219
226A -> 233A -0.48909
231A -> 234A 0.32214
231A -> 235A 0.15430
232A -> 234A -0.33018
232A -> 235A -0.18442
221B -> 229B -0.17245
227B -> 230B 0.49216
228B -> 230B -0.37277

Excited State 16: 5.415-A 1.7407 eV 712.28 nm f=0.0082 <S**2>=7.079
225A -> 233A -0.18885
226A -> 233A 0.74067
231A -> 234A 0.38164
232A -> 234A -0.38591

221B -> 229B 0.19686
227B -> 230B 0.16935
228B -> 230B -0.15539

Excited State 17: 5.429-A 1.7508 eV 708.14 nm f=0.0044 <S**2>=7.117
226A -> 233A 0.26487
231A -> 234A -0.46708
231A -> 235A 0.20329
232A -> 234A 0.47448
232A -> 235A -0.21658
227B -> 230B 0.43055
228B -> 230B -0.39725

Excited State 18: 5.436-A 1.8148 eV 683.19 nm f=0.0058 <S**2>=7.138
224A -> 233A -0.17672
225A -> 233A 0.16182
226A -> 233A -0.13255
217B -> 229B 0.10615
220B -> 229B 0.80860
221B -> 229B 0.40519
228B -> 230B -0.24289

Excited State 19: 5.336-A 1.8729 eV 662.01 nm f=0.0053 <S**2>=6.868
225A -> 233A 0.11493
231A -> 235A 0.14081
232A -> 235A -0.12401
220B -> 229B 0.15676
221B -> 229B 0.16208
227B -> 230B 0.51964
228B -> 230B 0.77369

Excited State 20: 5.136-A 1.9023 eV 651.74 nm f=0.1437 <S**2>=6.345
222A -> 233A -0.11465
225A -> 233A 0.71294
231A -> 233A -0.10775
220B -> 229B -0.41154
221B -> 229B 0.43542
224B -> 230B -0.14451

Excited State 21: 5.326-A 1.9831 eV 625.20 nm f=0.0083 <S**2>=6.843
222A -> 233A 0.18326
224A -> 233A 0.87553
225A -> 233A 0.19612
219B -> 229B -0.26738
220B -> 229B 0.19219

Excited State 22: 5.614-A 2.0445 eV 606.43 nm f=0.0074 <S**2>=7.629
222A -> 233A -0.54471
224A -> 233A 0.31217
232A -> 235A 0.11166
217B -> 229B -0.23381
219B -> 229B 0.63696
221B -> 229B -0.10470

Excited State 23: 5.396-A 2.1076 eV 588.27 nm f=0.0216 <S**2>=7.028
222A -> 233A 0.13731
228A -> 234A 0.16849
228A -> 235A 0.12160
231A -> 234A 0.38027
231A -> 235A -0.13573
232A -> 234A 0.44326
232A -> 235A 0.50676
217B -> 229B 0.12546
224B -> 230B 0.36431
225B -> 230B 0.10493
226B -> 230B -0.12208
227B -> 230B 0.23416

Excited State 24: 5.408-A 2.1275 eV 582.76 nm f=0.0119 <S**2>=7.061
221A -> 233A -0.12956
222A -> 233A -0.11138
223A -> 233A 0.15435
228A -> 234A 0.11313
228A -> 235A -0.11889
231A -> 234A 0.53988

231A -> 235A 0.19162
232A -> 234A 0.52545
232A -> 235A -0.27622
217B -> 229B -0.16470
224B -> 230B -0.30950
227B -> 230B -0.20421

Excited State 25: 5.421-A 2.1433 eV 578.46 nm f=0.0200 <S**2>=7.096
220A -> 233A 0.11165
221A -> 233A 0.18399
223A -> 233A -0.23499
224A -> 233A 0.12019
228A -> 235A -0.16420
231A -> 235A -0.14673
232A -> 235A 0.19905
213B -> 229B -0.10333
214B -> 229B -0.13414
217B -> 229B 0.26904
219B -> 229B 0.12295
224B -> 230B -0.43695
225B -> 230B -0.24089
226B -> 230B 0.48321
227B -> 230B 0.27111

Excited State 26: 5.352-A 2.1760 eV 569.78 nm f=0.0094 <S**2>=6.912
223A -> 233A 0.77819
223A -> 234A 0.10609
231A -> 234A -0.11929
232A -> 235A 0.43100
216B -> 229B 0.10278
217B -> 229B -0.12679
224B -> 230B -0.10732
226B -> 230B 0.12936
227B -> 230B 0.12807

Excited State 27: 5.388-A 2.1988 eV 563.88 nm f=0.0039 <S**2>=7.007
223A -> 233A 0.28306
228A -> 234A 0.15520
231A -> 235A -0.25690
232A -> 235A -0.42304
224B -> 230B 0.46053
225B -> 230B -0.39784
226B -> 230B 0.41940

Excited State 28: 5.445-A 2.2224 eV 557.89 nm f=0.0022 <S**2>=7.161
212A -> 234A 0.11299
221A -> 233A 0.36378
223A -> 233A 0.30831
223A -> 234A 0.13013
224A -> 233A 0.15530
231A -> 235A -0.30513
232A -> 235A -0.28228
217B -> 229B 0.38687
219B -> 229B 0.12844
224B -> 230B -0.16251
225B -> 230B 0.31347
226B -> 230B -0.37942

Excited State 29: 5.283-A 2.2405 eV 553.37 nm f=0.0017 <S**2>=6.727
212A -> 234A -0.30077
213A -> 234A -0.31651
214A -> 234A -0.12718
216A -> 234A 0.15830
220A -> 233A 0.26031
221A -> 234A -0.10498
223A -> 233A 0.11315
223A -> 234A -0.33154
228A -> 234A 0.53207
228A -> 235A -0.12069
229A -> 234A -0.14428
230A -> 234A -0.17926
231A -> 234A -0.10596
232A -> 235A 0.10551
213B -> 229B -0.14941
214B -> 229B -0.13190

224B -> 230B -0.18024
225B -> 230B 0.11735

Excited State 30: 5.254-A 2.2461 eV 551.99 nm f=0.0089 <S**2>=6.652
203A -> 234A -0.10389
212A -> 234A 0.30997
213A -> 234A 0.20706
216A -> 234A -0.14034
220A -> 233A -0.14072
222A -> 234A -0.12550
223A -> 233A -0.13732
223A -> 234A 0.36110
228A -> 234A 0.64856
229A -> 234A -0.29059
231A -> 234A -0.15014