Supporting Information

Theoretical study of luminescent vapochromic compound including an $AuCu_2(NHC)_2$ core†

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Table S1: Explanation of computational methods and DFT functional

Method

Method	Explanation
DFT	Density functional method. This is very useful for transition metal complexes. This is not very powerful to evaluate dispersion interaction with usual functional.
SCS-MP2	Spin-component scaled Möller-Plesset perturbation theory proposed by Grimme (J. Chem. Phys.118, 9095 (2003)). This method presents a similar result to high quality CCSD(T) method in many cases.
MP2	The second order Möller-Plesset perturbation theory. This is the most simple method to incorporate the electron correlation effect. This is useful to evaluate dynamical correlation.
MP4	The forth order Möller-Plesset perturbation theory. This is much better than MP2. This is also useful to evaluate dynamical correlation. The quality is corresponding to the single-double configuration interaction method which is based on variational principle.
B3PW91	One kind of DFT Hybrid functional, which is similar well known B3LYP. In our experience, this tends to provide better results than B3LYP in transition metal complexes. Reference is presented in the manual of Gaussian 09.
LC-BLYP	Long-range corrected BLYP functional. The Hartree-Fock exchange term is introduced in a dependent way on the distance. This is useful for calculating charge-transfer system. Reference is presented in the manual of Gaussian 09.
M06	Hybrid functional proposed by Truhlar group. Parameters used in this functional were well optimized to incorporate even non-covalent interaction. Reference is presented in the manual of Gaussian 09.

M06L	Pure functional proposed by Truhlar group. Parameters used in this functional were well optimized to incorporate even non-covalent interaction. This is believed to be useful for metallic system. Reference is presented in the manual of Gaussian 09.
M06-2X	Hybrid functional proposed by Truhlar group. Parameters used in this functional were well optimized to incorporate even non-covalent interaction. In particular, this is useful to incorporate dispersion interaction. Reference is presented in the manual of Gaussian 09.
M06-HF	Hybrid functional proposed by Truhlar group. Parameters used in this functional were well optimized to incorporate even non-covalent interaction. Hartree-Fock exchange is 100%. Reference is presented in the manual of Gaussian 09.

Table S2. Optimized geometrical parameters of $[Au(im(CH_2Py)_2)_2(CuL_2)_2]^{3+}$ (L=MeCN(**1**) and MeOH(**2**)) [a]

	B3PW91	LC-BLYP	M06L	M06	M06-2X	M06-HF	SCS-MP2	expl.
1								
Au-Cu	4.742	4.672	4.641	4.628	4.713	4.787	4.631	4.591
Au-C	2.027	2.022	2.043	2.057	2.045	2.006	2.032	2.012
Cu-N1(MeCN)	2.048	2.025	2.001	2.039	2.124	2.152	2.067	1.991
Cu-N2 (Py)	2.096	2.058	2.094	2.082	2.152	2.168	2.074	2.051
2								
Au-Cu	3.176	3.164	2.866	2.960	2.976	2.820	2.767	2.792
Au-C1	2.038	2.029	2.053	2.068	2.052	2.052	2.043	2.017
Au-C2	2.034	2.026	2.056	2.064	2.059	2.010	2.036	2.009
Au-N1	1.974	1.940	1.976	1.960	2.064	2.124	2.021	1.965
Au-N2	1.972	1.941	1.966	1.963	2.065	2.126	2.019	1.956
Cu-O	2.328	2.263	2.290	2.352	2.216	2.159	2.190	2.120

[a] Bond distances are in Å. We found that MeOH molecule near the MeOH coordinating with the Cu center, in the X-ray structure. The presence of the hydrogen bonded MeOH improved the optimized Cu-O distance.

Table S3. TD-DFT-calculated transition energies from S_0 to T_N state (N=1-10) in **1** at the S_0 structure

complex	eV	character
1	3.25	21.9 % (Cu d)$_{202}$→(Py π*)$_{205}$, 22.0 % (Cu d)$_{203}$→(Py π*)$_{207}$
	3.25	21.8 % (Cu d)$_{202}$→(Py π*)$_{207}$, 22.0 % (Cu d)$_{203}$→(Py π*)$_{205}$
	3.39	17.8 % (Cu d)$_{202}$→(Py π*)$_{208}$,19.5 % (Cu d)$_{203}$→(Py π*)$_{206}$
	3.39	19.3 % (Cu d)$_{202}$→(Py π*)$_{206}$, 17.9 % (Cu d)$_{203}$→(Py π*)$_{208}$
	3.45	22.1 % (Cu d)$_{200}$→(Py π*)$_{207}$, 22.5 % (Cu d)$_{201}$→(Py π*)$_{205}$
	3.45	22.3 % (Cu d)$_{200}$→(Py π*)$_{205}$, 22.3 % (Cu d)$_{201}$→(Py π*)$_{207}$
	3.52	20.1 % (Cu d)$_{200}$→(Py π*)$_{206}$, 18.5 % (Cu d)$_{201}$→(Py π*)$_{208}$
	3.52	18.5 % (Cu d)$_{200}$→(Py π*)$_{208}$, 20.1 % (Cu d)$_{201}$→(Py π*)$_{206}$
	3.66	5.4 % (Cu d)$_{198}$→(Py π*)$_{205}$, 5.3 % (Cu d)$_{199}$→(Py π*)$_{207}$, 37.5 % (Cu d)$_{203}$→(carben π* + Au p)$_{204}$
	3.67	5.5 % (Cu d)$_{198}$→(Py π*)$_{207}$, 5.5 % (Cu d)$_{199}$→(Py π*)$_{205}$, 37.1 % (Cu d)$_{202}$→(carben π* + Au p)$_{204}$

Table S4. TD-DFT-calculated transition energies from S_0 to T_N state (N=1-10) in **2** at the S_0 structure

complex	eV	character
2	2.79	31.3 % (Au d –Cu d)$_{177}$→(Au–Cu metal bond)$_{178}$, 15.3 %(Au d – Cu d)$_{177}$→(Au p – Cu d)$_{179}$
	3.08	24.7 % (Cu d)$_{176}$→(Au–Cu metal bond)$_{178}$, 18.3 %(Cu d)$_{176}$→(Au p – Cu d)$_{179}$
	3.13	34.3 % (Cu d)$_{175}$→(Au–Cu metal bond)$_{178}$, 11.1 %(Cu d)$_{175}$→(Au p – Cu d)$_{179}$
	3.13	33.5 % (Cu d)$_{174}$→(Au–Cu metal bond)$_{178}$, 11.4 %(Cu d)$_{174}$→(Au p – Cu d)$_{179}$
	3.26	5.4 %(Cu d)$_{176}$→(Py π*)$_{180}$, 12.3 %(Au d –Cu d)$_{177}$→(Au–Cu metal bond)$_{178}$, 21.9 %(Au d –Cu d)$_{177}$→(Au p – Cu d)$_{179}$
	3.36	30.3 % (Au d –Cu d)$_{173}$→(Au–Cu metal bond)$_{178}$, 10.5 % (Au d –Cu d)$_{173}$→(Au p – Cu d)$_{179}$
	3.39	14.5 % (Cu d)$_{176}$→(Au–Cu metal bond)$_{178}$, 8.9 % (Cu d)$_{176}$→(Au p – Cu d)$_{179}$, 15.4 % (Au d –Cu d)$_{177}$→(Py π*)$_{180}$
	3.48	9.1 % (Cu d)$_{174}$→(Py π*)$_{180}$, 5.7 % (Cu d)$_{175}$→(Au–Cu metal bond)$_{178}$, 16.6 % (Cu d)$_{175}$→(Au p – Cu d)$_{179}$
	3.48	5.2 % (Cu d)$_{174}$→(Au–Cu metal bond)$_{178}$, 14.8 % (Cu d)$_{174}$→(Au p – Cu d)$_{179}$, 10.5 % (Cu d)$_{175}$→(Py π*)$_{180}$
	3.62	5.8 % (Cu d)$_{175}$→(Py π*)$_{182}$, 4.5 % (Cu d)$_{176}$→(Py π*)$_{181}$, 6.3 % (Au d –Cu d)$_{177}$→(Py π*)$_{182}$

Table S5. Optimized geometrical parameters of $[Au(im(CH_2Py)_2)_2(CuL_2)_2]^{3+}$ (L=MeCN(**1**) and MeOH(**2**)) [a] in the S_0 state and T_1 state

State	T_1				S_0
1	Py^{L1} [b]	Py^{L2}	Py^{R1}	Py^{R2}	
N1-C2	1.379	1.379	1.348	1.348	1.347
N1-C6	1.370	1.370	1.347	1.348	1.347
C2-C3	1.384	1.384	1.394	1.394	1.394
C3-C4	1.398	1.398	1.391	1.391	1.391
C4-C5	1.403	1.403	1.392	1.392	1.392
C5-C6	1.375	1.375	1.388	1.388	1.388
Cu-N1 of Py	1.954	1.954	2.076	2.076	2.074
Cu-N2 of MeCN	2.072	2.072	2.067	2.067	2.067

State	T_1				S_0	
2	Py^{L1}	Py^{L2}	Py^{R1}	Py^{R2}	Py^{L1}, Py^{R1}	Py^{L1},Py^{R2}
N1-C2	1.352	1.352	1.352	1.352	1.351	1.351
N1-C6	1.347	1.347	1.347	1.347	1.348	1.348
C2-C3	1.392	1.392	1.392	1.392	1.392	1.392
C3-C4	1.394	1.394	1.394	1.394	1.394	1.394
C4-C5	1.390	1.390	1.390	1.390	1.391	1.390
C5-C6	1.390	1.390	1.390	1.390	1.390	1.390
Cu-N1 (Py)	2.104	2.072	2.104	2.072	2.021	2.019
Cu-O	2.129		2.131		2.189	

[a] Bond distances are in Å [b]See Scheme 1 for Py^{L1}, Py^{R1} etc.

Table S6. Binding energies[a] of MeCN with the Cu center of $[CuPy_2(MeCN)]^+$ (in kcal/mol)

	BE
MP2	-35.2
MP3	-26.2
MP4(DQ)	-32.4
MP4(SDQ)	-38.1
MP4(SDTQ)	-44.7
SCS-MP2	-31.8
CCSD	-30.0
CCSD(T)	-32.6
B3PW91	-31.4
LC-BLYP	-35.9
M06L	-34.9
M06	-32.5
M06-2X	-28.3
M06-HF	-25.9

[a] BS-II was employed. The compound is shown in Scheme 2

Table S7. Cartesian coordinates for the of $[Au(im(CH_2Py)_2)_2(CuL_2)_2]^{3+}$ (L=MeCN(**1**) and MeOH(**2**)) in the S_0 state calculated by SCS-MP2 method

Structure **1**

Au	0.00000000	0.00000000	0.00000000
C	1.71360600	1.09288700	0.00000000
N	2.39713200	1.55757600	1.07444500
C	3.48605600	2.31127100	0.67891300
N	2.39713200	1.55757600	-1.07444500
C	3.48605600	2.31127100	-0.67891300
C	2.04782400	1.24747900	2.45817800
H	4.14731600	2.79407400	1.38321500
C	2.04782400	1.24747900	-2.45817800
H	4.14731600	2.79407400	-1.38321500
H	0.96158600	1.31298100	2.56643900
H	2.48619200	2.02653100	3.09112800
H	0.96158600	1.31298100	-2.56643900
H	2.48619200	2.02653100	-3.09112800
C	2.51497000	-0.12414700	2.90383800
C	3.74576600	-0.64282100	2.50545600
H	4.38743400	-0.07264200	1.84074300
N	1.69616000	-0.79251700	3.73953400
C	2.09420400	-1.99938700	4.18564800
C	3.30037800	-2.58637600	3.82925000
C	4.14797100	-1.89010200	2.97272700
H	5.10765100	-2.30608500	2.68014400
H	3.56652700	-3.56196800	4.22263700
H	1.40757500	-2.50062700	4.86014700
C	2.51497000	-0.12414700	-2.90383800
C	3.74576600	-0.64282100	-2.50545600
H	4.38743400	-0.07264200	-1.84074300
N	1.69616000	-0.79251700	-3.73953400
C	2.09420400	-1.99938700	-4.18564800
C	3.30037800	-2.58637600	-3.82925000
C	4.14797100	-1.89010200	-2.97272700
H	5.10765100	-2.30608500	-2.68014400

H	3.56652700	-3.56196800	-4.22263700
H	1.40757500	-2.50062700	-4.86014700
C	-1.71360600	-1.09288700	0.00000000
N	-2.39713200	-1.55757600	1.07444500
C	-3.48605600	-2.31127100	0.67891300
N	-2.39713200	-1.55757600	-1.07444500
C	-3.48605600	-2.31127100	-0.67891300
C	-2.04782400	-1.24747900	2.45817800
H	-4.14731600	-2.79407400	1.38321500
C	-2.04782400	-1.24747900	-2.45817800
H	-4.14731600	-2.79407400	-1.38321500
H	-0.96158600	-1.31298100	2.56643900
H	-2.48619200	-2.02653100	3.09112800
H	-0.96158600	-1.31298100	-2.56643900
H	-2.48619200	-2.02653100	-3.09112800
C	-2.51497000	0.12414700	2.90383800
C	-3.74576600	0.64282100	2.50545600
H	-4.38743400	0.07264200	1.84074300
N	-1.69616000	0.79251700	3.73953400
C	-2.09420400	1.99938700	4.18564800
C	-3.30037800	2.58637600	3.82925000
C	-4.14797100	1.89010200	2.97272700
H	-5.10765100	2.30608500	2.68014400
H	-3.56652700	3.56196800	4.22263700
H	-1.40757500	2.50062700	4.86014700
C	-2.51497000	0.12414700	-2.90383800
C	-3.74576600	0.64282100	-2.50545600
H	-4.38743400	0.07264200	-1.84074300
N	-1.69616000	0.79251700	-3.73953400
C	-2.09420400	1.99938700	-4.18564800
C	-3.30037800	2.58637600	-3.82925000
C	-4.14797100	1.89010200	-2.97272700
H	-5.10765100	2.30608500	-2.68014400
H	-3.56652700	3.56196800	-4.22263700
H	-1.40757500	2.50062700	-4.86014700
Cu	0.00000000	0.00000000	4.63139300

Cu	0.00000000	0.00000000	-4.63139300
N	-0.70371000	-1.43183500	5.94595500
C	-1.11834300	-2.04866800	6.83592600
C	-1.63455700	-2.81703400	7.95606500
H	-0.86640300	-2.91187100	8.73024600
H	-1.92826300	-3.81823600	7.62539900
H	-2.50774200	-2.31426300	8.38406600
N	0.70371000	1.43183500	5.94595500
C	1.11834300	2.04866800	6.83592600
C	1.63455700	2.81703400	7.95606500
H	0.86640300	2.91187100	8.73024600
H	1.92826300	3.81823600	7.62539900
H	2.50774200	2.31426300	8.38406600
N	-0.70371000	-1.43183500	-5.94595500
C	-1.11834300	-2.04866800	-6.83592600
C	-1.63455700	-2.81703400	-7.95606500
H	-0.86640300	-2.91187100	-8.73024600
H	-1.92826300	-3.81823600	-7.62539900
H	-2.50774200	-2.31426300	-8.38406600
N	0.70371000	1.43183500	-5.94595500
C	1.11834300	2.04866800	-6.83592600
C	1.63455700	2.81703400	-7.95606500
H	0.86640300	2.91187100	-8.73024600
H	1.92826300	3.81823600	-7.62539900
H	2.50774200	2.31426300	-8.38406600

Structure **2**

Au	0.00000000	0.00000000	0.00000000
C	2.04260000	0.00000000	0.00000000
N	2.86939400	0.00000000	1.07477800
C	4.19221200	0.00000000	0.67780000
N	2.86939400	0.00000000	-1.07477800
C	4.19221200	0.00000000	-0.67780000
C	2.44306400	0.11576300	2.47273700
H	5.01322100	0.00556600	1.37898900
C	2.44306400	-0.11576300	-2.47273700

H	5.01322100	-0.00556600	-1.37898900
H	1.42307900	-0.27192500	2.54081200
H	3.09209500	-0.52522600	3.07503200
H	1.42307900	0.27192500	-2.54081200
H	3.09209500	0.52522600	-3.07503200
C	2.50153400	1.54582100	2.95556800
C	3.61482700	2.01865700	3.64473200
H	4.42567100	1.34094600	3.89543600
N	1.45352900	2.34454100	2.65644500
C	1.52742000	3.64243400	3.01260400
C	2.61395900	4.19100900	3.68304200
C	3.67681800	3.35957200	4.01932900
H	4.53636300	3.74324700	4.56096700
H	2.61294600	5.24428200	3.94433500
H	0.66984900	4.25679200	2.75466500
C	2.50153400	-1.54582100	-2.95556800
C	3.61482700	-2.01865700	-3.64473200
H	4.42567100	-1.34094600	-3.89543600
N	1.45352900	-2.34454100	-2.65644500
C	1.52742000	-3.64243400	-3.01260400
C	2.61395900	-4.19100900	-3.68304200
C	3.67681800	-3.35957200	-4.01932900
H	4.53636300	-3.74324700	-4.56096700
H	2.61294600	-5.24428200	-3.94433500
H	0.66984900	-4.25679200	-2.75466500
C	-2.03560000	0.00000000	0.00000000
N	-2.86018100	-0.42620000	0.98686500
C	-4.18322500	-0.26910600	0.62311500
N	-2.86018100	0.42620000	-0.98686500
C	-4.18322500	0.26910600	-0.62311500
C	-2.41341200	-0.94560700	2.27885100
H	-5.00331500	-0.54013900	1.27165900
C	-2.41341200	0.94560700	-2.27885100
H	-5.00331500	0.54013900	-1.27165900
H	-1.35469600	-1.19769500	2.16845000
H	-2.95893700	-1.87036300	2.48402800

H	-1.35469600	1.19769500	-2.16845000
H	-2.95893700	1.87036300	-2.48402800
C	-2.61056400	0.03600600	3.40919100
C	-3.51950100	-0.23692600	4.42684200
H	-4.09142100	-1.16008000	4.40934900
N	-1.86444000	1.16222200	3.39749800
C	-2.03160600	2.03761600	4.40925600
C	-2.92389100	1.83789100	5.45604100
C	-3.68234100	0.67337500	5.47023300
H	-4.38444300	0.47312600	6.27419100
H	-3.00804800	2.58066000	6.24272500
H	-1.41422000	2.93060200	4.38083900
C	-2.61056400	-0.03600600	-3.40919100
C	-3.51950100	0.23692600	-4.42684200
H	-4.09142100	1.16008000	-4.40934900
N	-1.86444000	-1.16222200	-3.39749800
C	-2.03160600	-2.03761600	-4.40925600
C	-2.92389100	-1.83789100	-5.45604100
C	-3.68234100	-0.67337500	-5.47023300
H	-4.38444300	-0.47312600	-6.27419100
H	-3.00804800	-2.58066000	-6.24272500
H	-1.41422000	-2.93060200	-4.38083900
Cu	-0.39530900	1.72105200	2.13038800
Cu	-0.39530900	-1.72105200	-2.13038800
O	-1.14875100	3.41482400	0.96551300
H	-0.52745600	3.92237900	0.42313000
C	-2.34311600	4.19812300	1.16806700
H	-2.12660500	5.09963600	1.74953900
H	-3.03797100	3.56560200	1.72070700
H	-2.78793300	4.47528000	0.20811800
O	-1.14875100	-3.41482400	-0.96551300
H	-0.52745600	-3.92237900	-0.42313000
C	-2.34311600	-4.19812300	-1.16806700
H	-2.12660500	-5.09963600	-1.74953900
H	-3.03797100	-3.56560200	-1.72070700
H	-2.78793300	-4.47528000	-0.20811800

Table S8. Cartesian coordinates for the of $[Au(im(CH_2Py)_2)_2(CuL_2)_2]^{3+}$ (L=MeCN(**1**) and MeOH(**2**)) in the T_1 state calculated by SCS-MP2 method

Structure **1**

Au	-0.06522939	-0.00011057	-0.00007393
C	-0.01997080	1.74015448	-1.04839841
N	-1.06997201	2.47775305	-1.48253005
C	-0.63886654	3.57169690	-2.20961413
N	1.07750019	2.39244462	-1.50739494
C	0.71766003	3.51716438	-2.22614377
C	-2.46390749	2.15865010	-1.18187791
H	-1.32089431	4.27560361	-2.66318564
C	2.45054093	1.97974857	-1.23640583
H	1.44353132	4.16739602	-2.69127965
H	-2.61468523	1.08532557	-1.32829846
H	-3.08567626	2.68064326	-1.91680634
H	2.45829061	0.87710156	-1.21997935
H	3.06122226	2.28056630	-2.09593818
C	-2.87607568	2.53335243	0.22751325
C	-2.48223033	3.73914094	0.80526036
H	-1.84989330	4.42656375	0.25146712
N	-3.67412869	1.65973603	0.87234626
C	-4.08397982	1.97596932	2.11565294
C	-3.72701726	3.15098037	2.76251852
C	-2.91099890	4.05626884	2.09016616
H	-2.62052468	4.99464586	2.55344662
H	-4.08964822	3.35004531	3.76565528
H	-4.72974948	1.24852384	2.59689657
C	3.00694578	2.51675000	0.06104271
C	2.52622974	3.66771380	0.65962670
H	1.70440126	4.20321795	0.19447189
N	4.04421238	1.80047751	0.61958784
C	4.61669912	2.30010362	1.75989294
C	4.17530619	3.44154006	2.38703982
C	3.09568426	4.15273751	1.84091119
H	2.72761654	5.06069285	2.30570858

H	4.68063672	3.78398889	3.28430208
H	5.45937123	1.74041298	2.14677788
C	-0.02000198	-1.74037291	1.04825490
N	-1.07001883	-2.47792973	1.48240623
C	-0.63894353	-3.57187774	2.20950347
N	1.07745737	-2.39271504	1.50721400
C	0.71758130	-3.51734820	2.22608278
C	-2.46395580	-2.15877124	1.18179880
H	-1.32098730	-4.27579979	2.66302629
C	2.45050084	-1.98000539	1.23627192
H	1.44344212	-4.16759198	2.69121843
H	-2.61473455	-1.08546517	1.32836181
H	-3.08571803	-2.68086394	1.91666138
H	2.45828146	-0.87735740	1.21998251
H	3.06117683	-2.28092538	2.09577173
C	-2.87613466	-2.53331693	-0.22762815
C	-2.48225056	-3.73902136	-0.80552188
H	-1.84984950	-4.42646800	-0.25183153
N	-3.67426564	-1.65967329	-0.87233120
C	-4.08417203	-1.97580529	-2.11564336
C	-3.72718135	-3.15073184	-2.76264926
C	-2.91106952	-4.05604005	-2.09043909
H	-2.62056497	-4.99435242	-2.55383123
H	-4.08986431	-3.34971407	-3.76578359
H	-4.73001035	-1.24834776	-2.59677669
C	3.00688644	-2.51684230	-0.06124027
C	2.52625076	-3.66779899	-0.65990240
H	1.70451667	-4.20346023	-0.19475715
N	4.04402198	-1.80040742	-0.61981834
C	4.61640191	-2.29980580	-1.76026716
C	4.17508283	-3.44122734	-2.38749396
C	3.09563894	-4.15263164	-1.84129258
H	2.72765020	-5.06060419	-2.30611804
H	4.68032474	-3.78350414	-3.28487219
H	5.45892889	-1.73991964	-2.14718135
Cu	-4.56522981	0.00000806	0.00009513

Cu	4.48482292	-0.00004837	0.00013029
N	-5.88143343	-0.77115460	1.39537875
C	-6.77997100	-1.19749463	1.99146429
C	-7.91035943	-1.72978565	2.73345492
H	-8.68660097	-0.96427305	2.83262384
H	-7.59361404	-2.04302595	3.73323557
H	-8.33018993	-2.59316379	2.20741003
N	-5.88147804	0.77132124	-1.39509795
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C	-7.91034626	1.73026676	-2.73303704
H	-8.68634982	0.96460062	-2.83288300
H	-7.59345693	2.04424390	-3.73254072
H	-8.33054167	2.59318620	-2.20653101
N	5.63974061	-0.65958615	1.58906955
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C	7.41015194	-1.67090933	3.21624444
H	7.06090247	-1.58740283	4.25058037
H	7.58038524	-2.72580876	2.97744150
H	8.35530865	-1.12699348	3.11552568
N	5.64054417	0.65936628	-1.58833804
C	6.42486714	1.11196752	-2.31009168
C	7.41063174	1.67125300	-3.21551476
H	7.06042018	1.58973854	-4.24968381
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H	8.35526547	1.12612694	-3.11644336

Structure **2**

Au	-1.09203085	0.03425619	-0.03319210
C	0.92250378	-0.03476671	0.14794924
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C	3.00428972	-0.37226949	0.96299961
N	1.85326774	0.35272926	-0.76440311
C	3.13498283	0.15018193	-0.27957899
C	1.06650336	-0.93910774	2.46804254
H	3.75293764	-0.67000433	1.68202201
C	1.54331293	0.84106868	-2.10405340

H	4.01904755	0.38997221	-0.85147500
H	0.01424728	-1.16397573	2.27304030
H	1.55807451	-1.87232259	2.75624844
H	0.48980465	1.13490399	-2.10131930
H	2.13883349	1.73852128	-2.29257001
C	1.20024713	0.07841236	3.57770251
C	2.05321682	-0.16400224	4.65069748
H	2.61400518	-1.09299625	4.69586669
N	0.47226016	1.21407340	3.49198220
C	0.60318669	2.12665626	4.47395176
C	1.43907512	1.95725676	5.57164296
C	2.17742552	0.78346096	5.66598415
H	2.83750326	0.60524150	6.50988385
H	1.49695013	2.72872883	6.33263493
H	0.00207425	3.02656060	4.37809159
C	1.80744203	-0.18799902	-3.17956080
C	2.84762920	-0.00339580	-4.08622551
H	3.46521068	0.88805100	-4.02627598
N	1.00591392	-1.27501636	-3.23065465
C	1.24690353	-2.19642222	-4.18299155
C	2.26935909	-2.08349088	-5.11792447
C	3.08586987	-0.95972492	-5.07250216
H	3.89249644	-0.82612451	-5.78744578
H	2.40946498	-2.85885976	-5.86412065
H	0.58222403	-3.05564969	-4.20065987
C	-3.11016980	0.09258450	-0.22486977
N	-4.04295053	-0.11549085	0.74086324
C	-5.32247625	0.00617526	0.22740460
N	-3.83017790	0.34516291	-1.34925056
C	-5.18858965	0.29495831	-1.08839553
C	-3.75027044	-0.33774248	2.15634922
H	-6.20833971	-0.12044736	0.83146544
C	-3.26302099	0.53972266	-2.68298230
H	-5.93563811	0.46550190	-1.84898843
H	-2.71610286	-0.68336204	2.22310194
H	-4.39715842	-1.14225458	2.51640986

H	-2.21281325	0.81124750	-2.55187074
H	-3.77382324	1.38452557	-3.15283704
C	-3.95914978	0.91095967	2.98259888
C	-5.10926914	1.06049091	3.75243932
H	-5.83848720	0.25672986	3.79563427
N	-3.01375725	1.87595813	2.92866220
C	-3.22256907	3.01403907	3.61772904
C	-4.35390536	3.23881216	4.39316775
C	-5.31454944	2.23714097	4.47151488
H	-6.20655718	2.36509841	5.07780322
H	-4.46519521	4.17623360	4.92846832
H	-2.44337827	3.76656395	3.54452233
C	-3.39597510	-0.69752414	-3.54137458
C	-4.38286545	-0.77440875	-4.51988975
H	-5.03300738	0.07689114	-4.69962248
N	-2.54784230	-1.72461188	-3.30959534
C	-2.69830465	-2.85228972	-4.02995307
C	-3.67092192	-3.00583542	-5.01099109
C	-4.52580183	-1.94082397	-5.27012095
H	-5.29027120	-2.01267011	-6.03828924
H	-3.74188917	-3.93854218	-5.56119398
H	-2.00207782	-3.65554158	-3.80941629
Cu	-1.10039647	1.65254444	2.16510164
Cu	-0.79891522	-1.61548370	-2.20404476
O	-0.60491781	3.71145242	1.94422765
H	0.34368731	3.90846874	1.98255512
C	-1.21887940	4.57501851	0.95927354
H	-1.02041851	5.62077029	1.20669550
H	-2.29159128	4.38642657	1.00377734
H	-0.84520007	4.34006000	-0.04130580
O	-0.46957360	-3.69988134	-1.91085817
H	0.45832679	-3.95357295	-1.78963928
C	-1.29403313	-4.53971423	-1.06954507
H	-1.11596621	-5.59161379	-1.30624536
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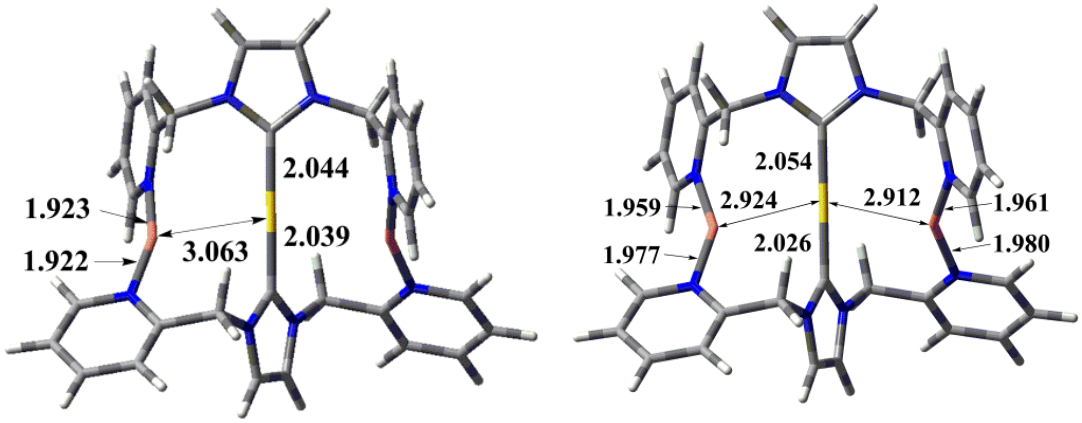


(A) S_0 state **(B) T_1 state**

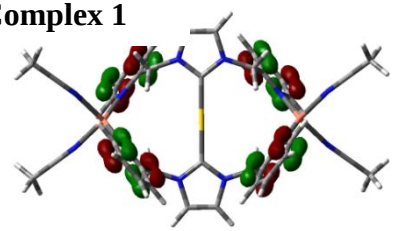
Figure S1. The Optimized structures of solvent free form in the S_0 state (A) and T_1 state (B)

The Au-Cu distance (3.063 Å) is moderately longer than that (2.767 Å) of the MeOH adduct. This is interesting, because one can expect that weak coordination of gas molecule leads to a short Au-Cu distance and no coordination leads to a shorter Au-Cu distance. This is reasonably explained based on bond angle and electron distribution. If the Cu center takes a three-coordinate structure like the MeOH adduct, the Py-Cu-Py angle is 126°. But, in the solvent free form, the Cu center takes a two-coordinate structure, in which an ideal Py-Cu-Py angle is about 180. Actually, the Py-Cu-Py angle increases to 160 in the solvent free form. As a result, the Au-Cu distance increases in the solvent free form; remember that the Py lone pair extends inside. Another reason is the Au-Cu electrostatic interaction. In the solvent free form, the Cu is two-coordinate but in the MeOH adduct, the Cu center received electron density from MeOH through σ-donation interaction. Hence, the Cu atomic population is more positively charged than in the MeOH adduct. Such positive charge induces the electrostatic repulsion with the positively charged Au center.

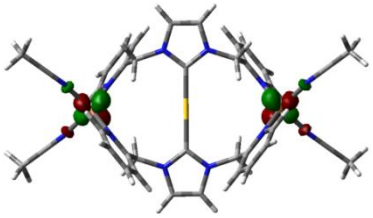
We also optimized the geometry at the T1 state, the electronic state of which is essentially the same as those of **2** and **3**. We employed here the DFT(B3PW91)/BS-II but did not the SCS-MP2 to optimize the Au-Cu distance due to the lack of computational time. Nevertheless, the emission spectrum was evaluated at 2.54 eV with the DFT(B3PW91)/BS-II, which is

not very different from the experimental value (2.16 eV). The assignment is the same as those of **2** and **3**.

Complex 1



HOMO-6



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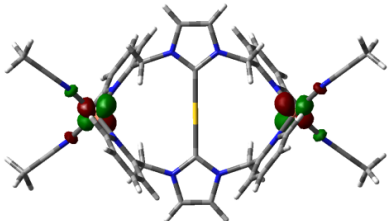

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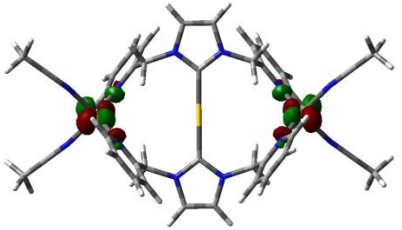
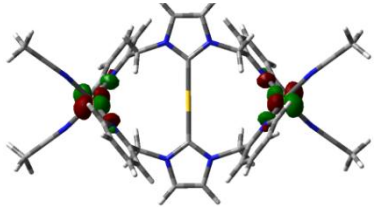
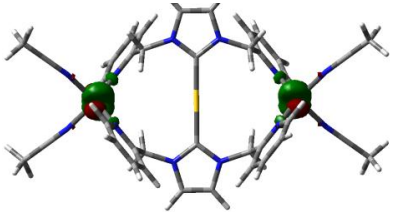


HOMO-3



HOMO-2



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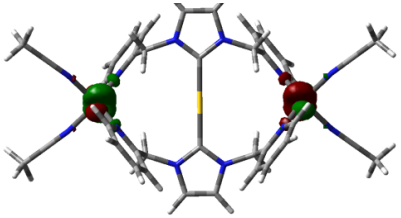
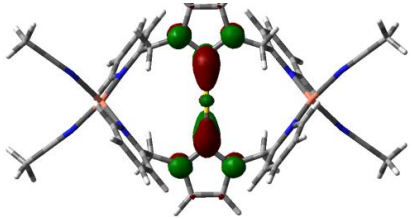


203(HOMO)



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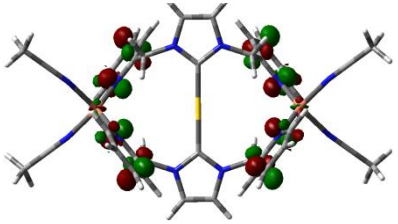

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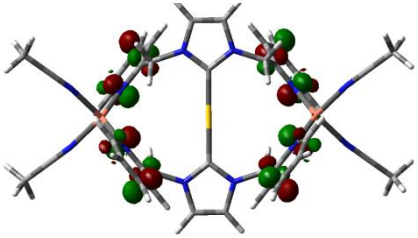

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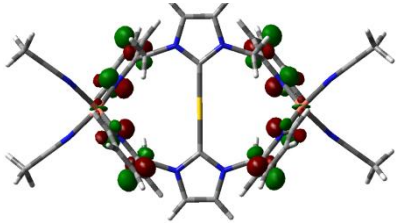

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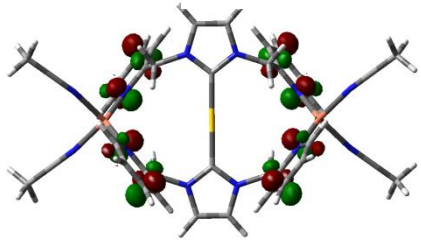
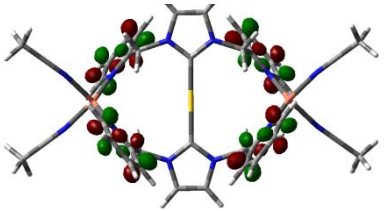


LUMO+4



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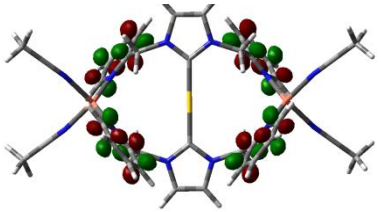
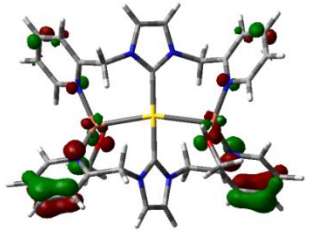
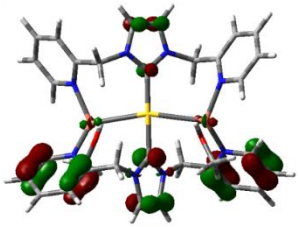


LUMO+6

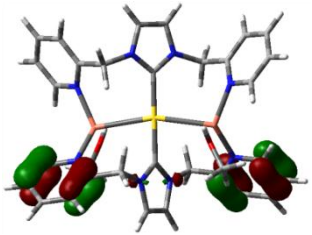
Complex 2



HOMO-22



HOMO-16



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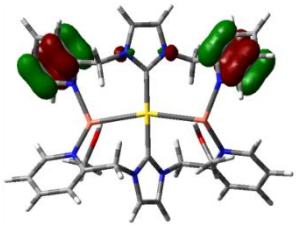
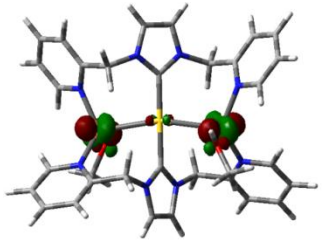
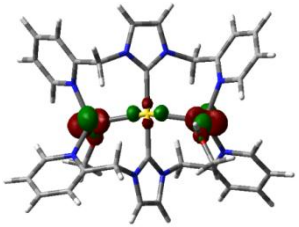


HOMO-13



HOMO-5



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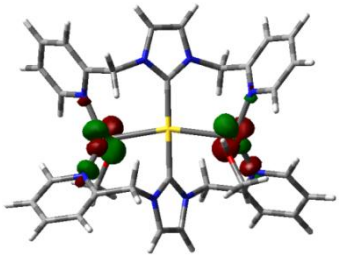

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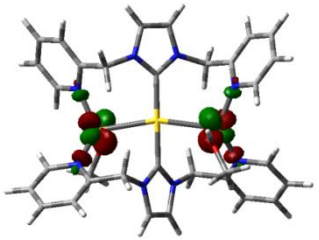

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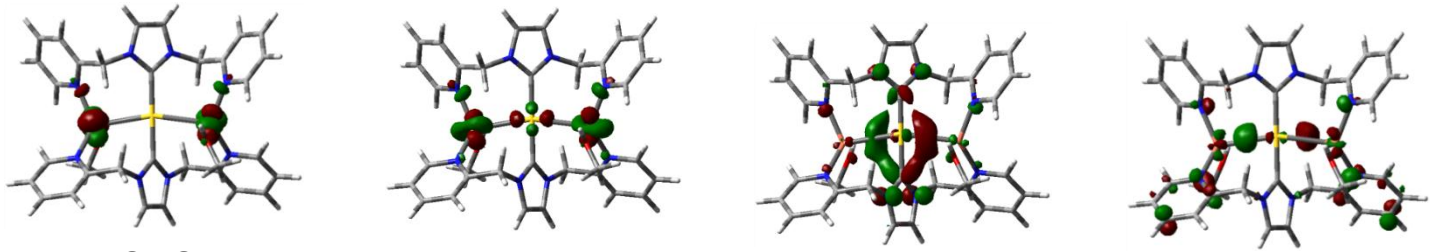
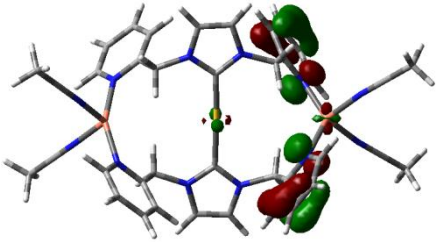


Figure S2. The frontier orbitals of **1** and **2** in the S_0 state

(A) Complex 1



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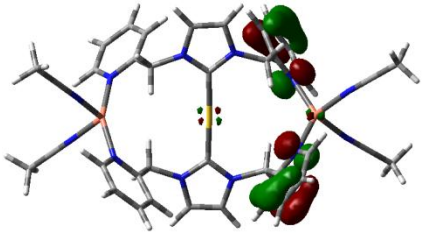
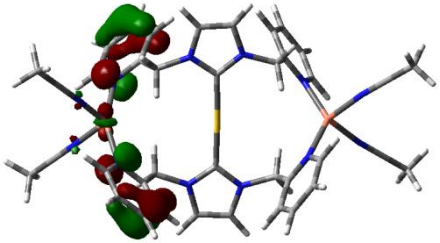
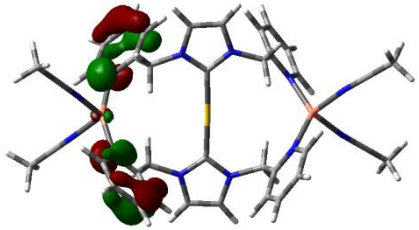


HOMO-19



HOMO-18



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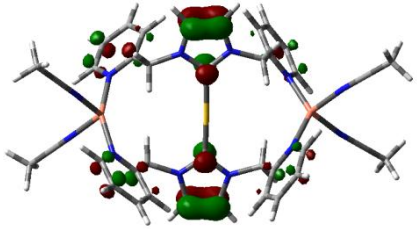

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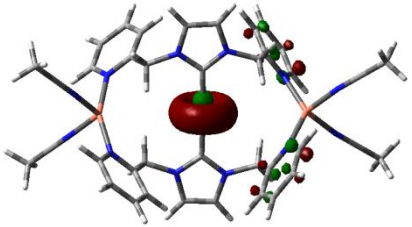
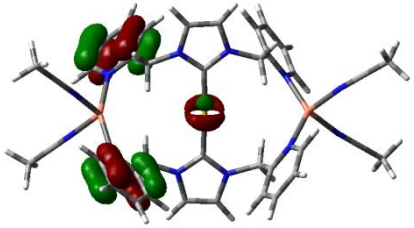
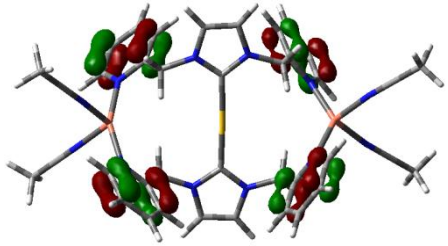


HOMO-15



HOMO-14



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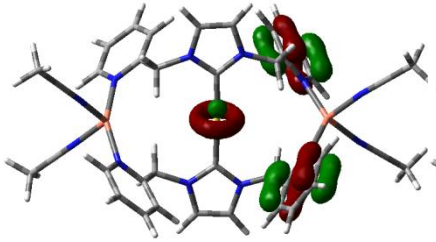

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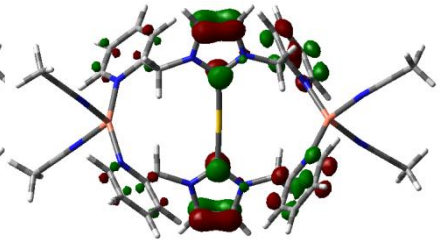

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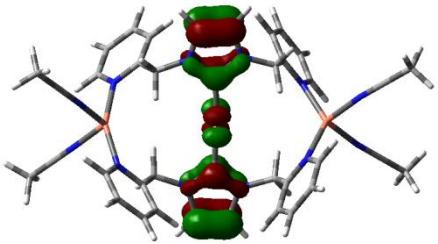

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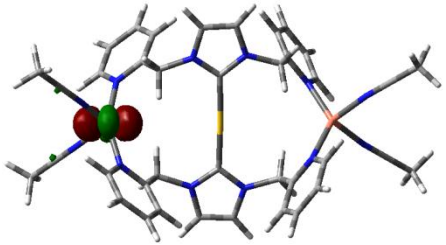

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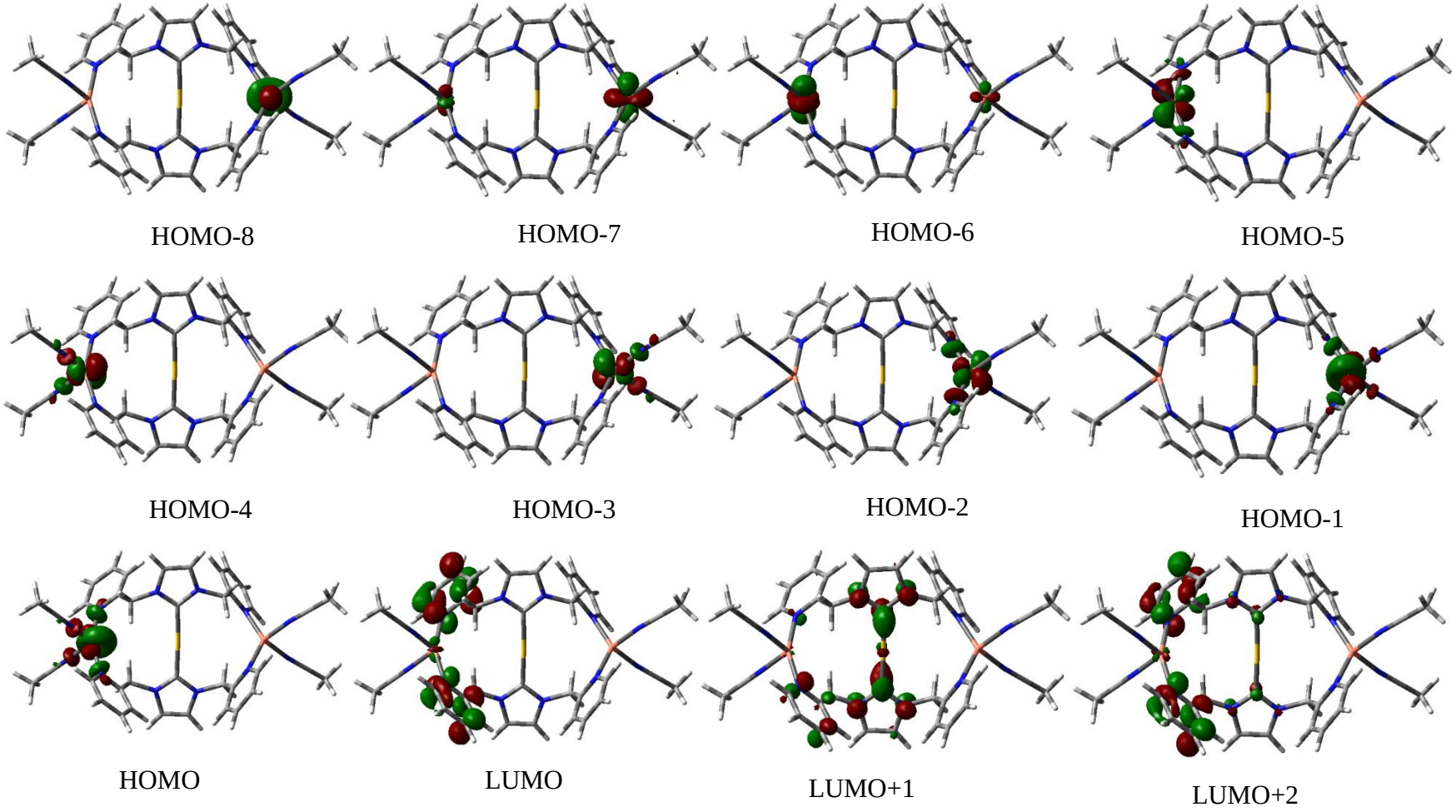
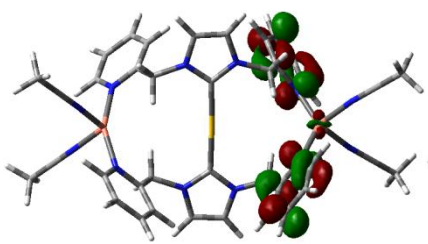
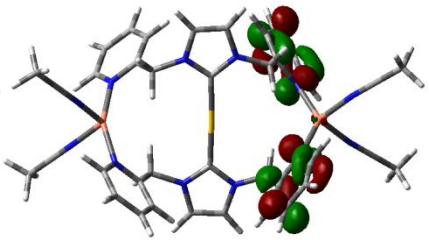




LUMO+3



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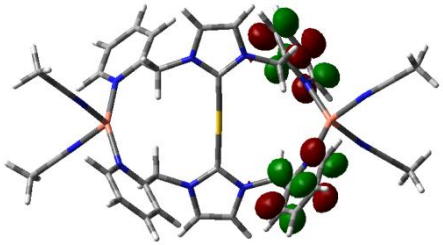

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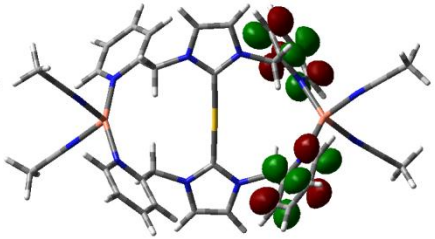
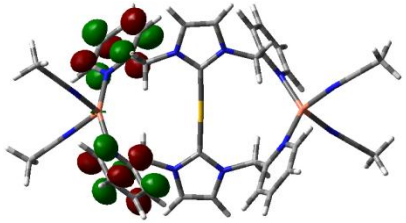
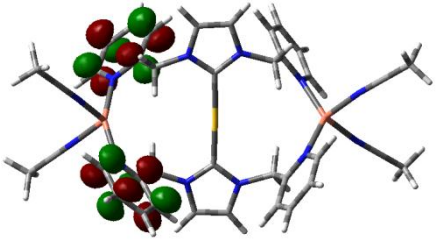


LUMO+6

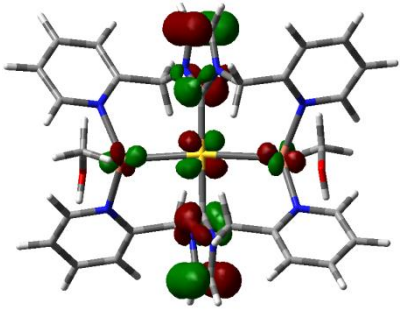


LUMO+7



LUMO+8

(B) Complex 2



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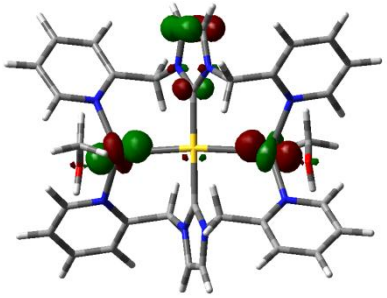
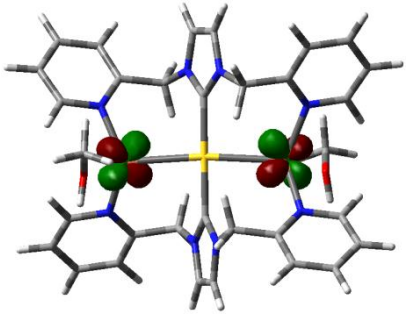


HOMO-9



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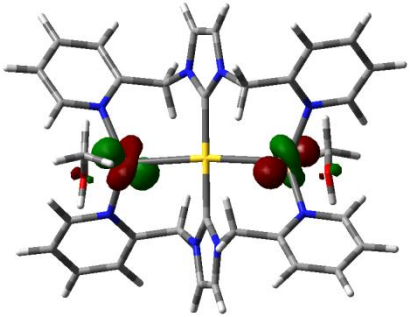

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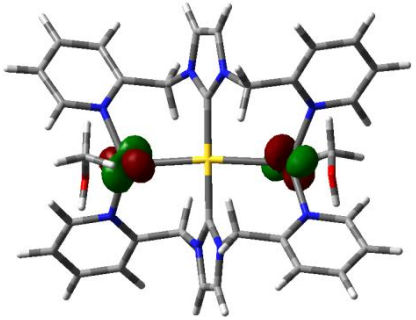

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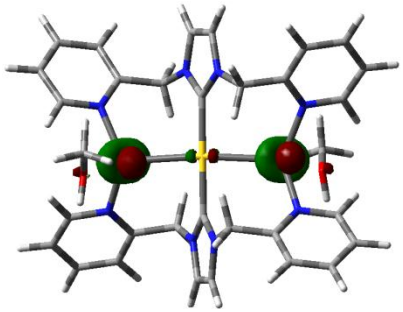

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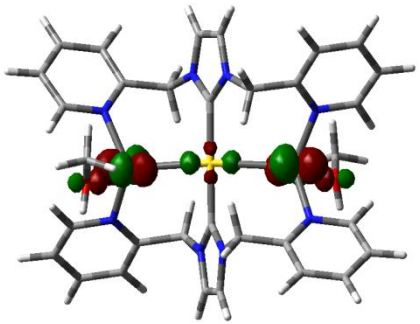

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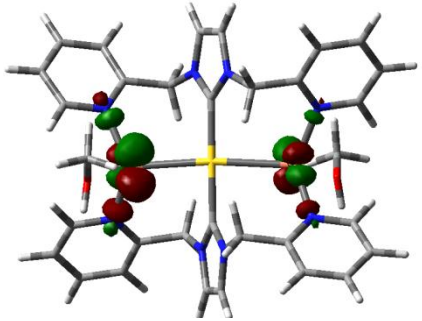

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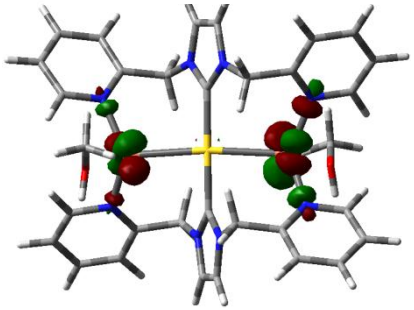
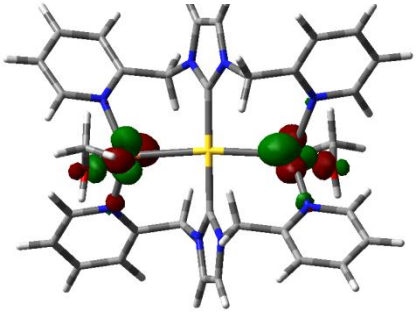
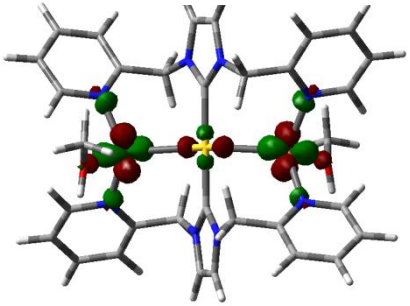


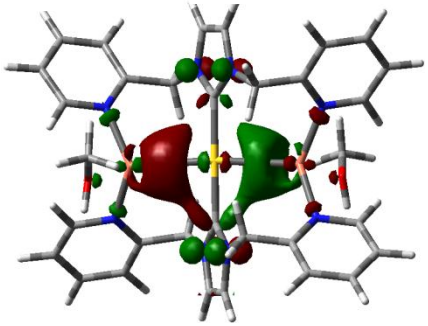
HOMO-2



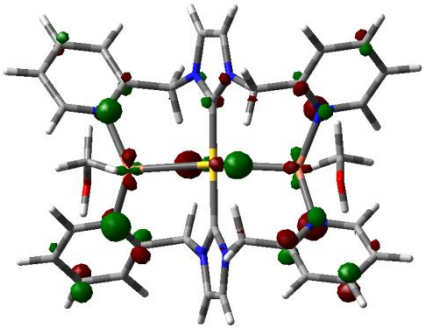
HOMO-1



HOMO



LUMO

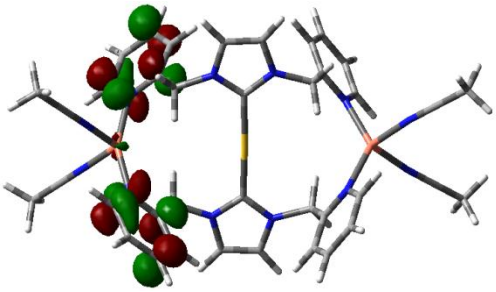


LUMO+1

Figure S3. The frontier orbitals of **1** and **2** in the S_0 state at the T_1 structure

Occupied α and β spin orbitals of **1** in the T_1 state

α orbitals



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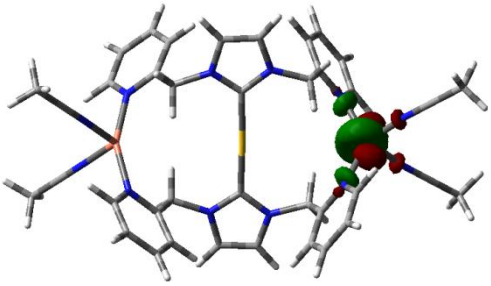

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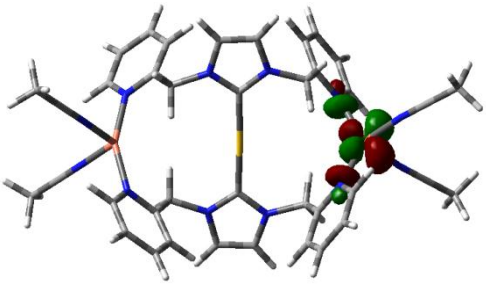

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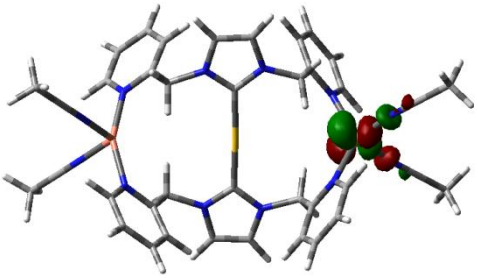

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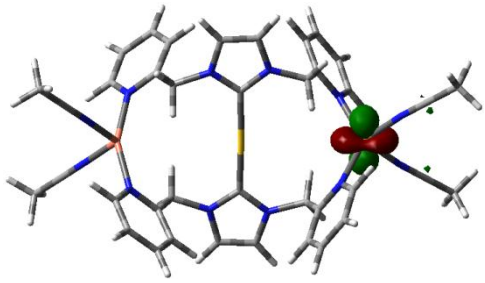
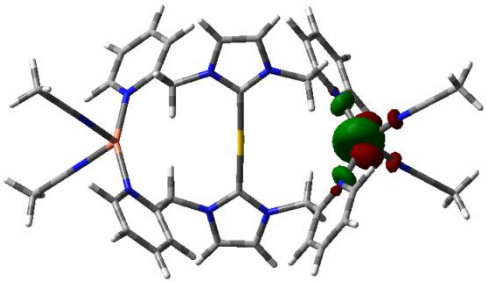


200

199

β orbitals



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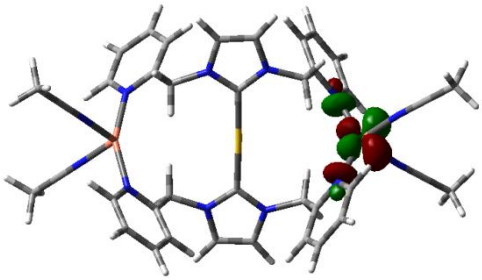

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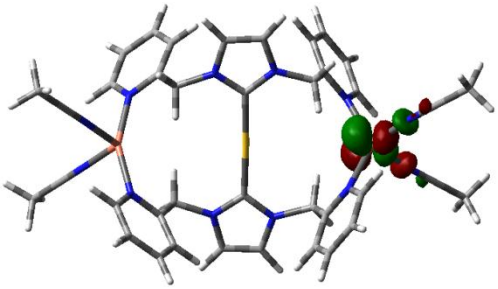

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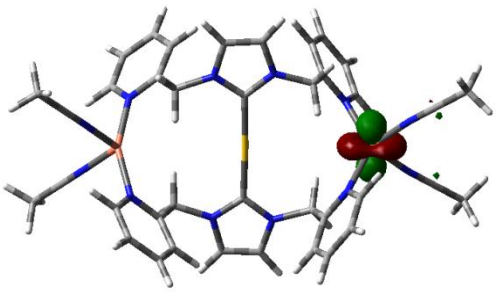

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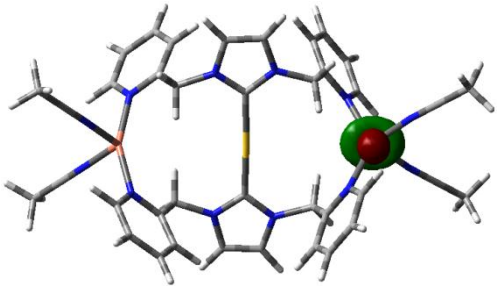

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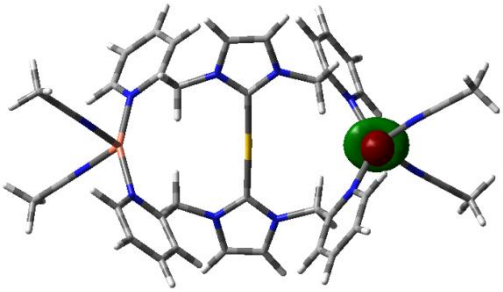

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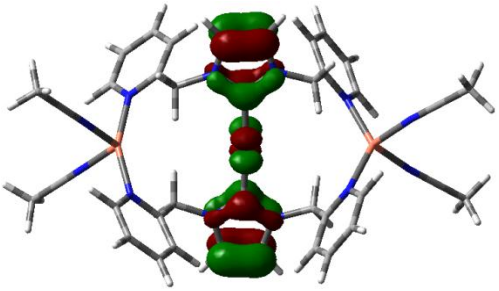

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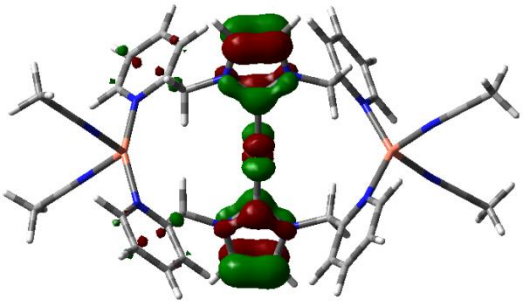

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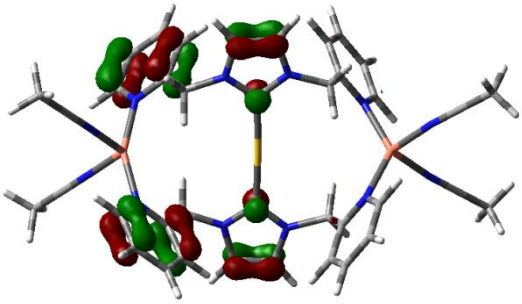

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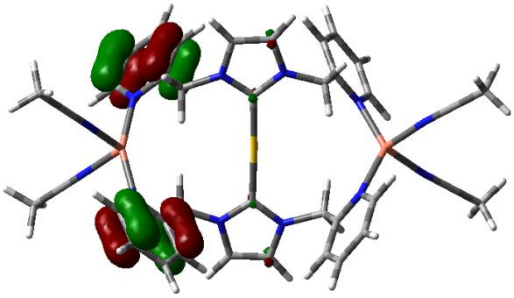

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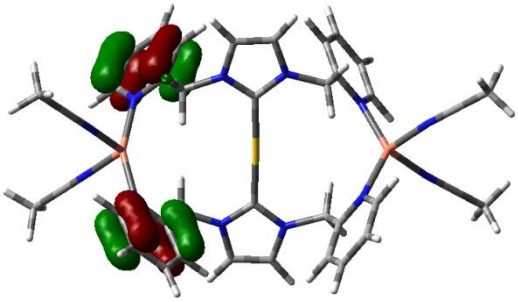

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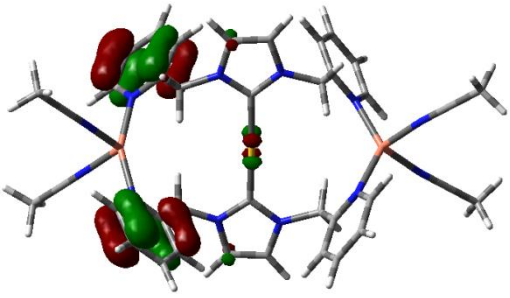

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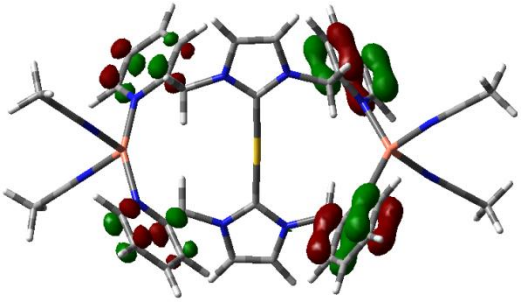

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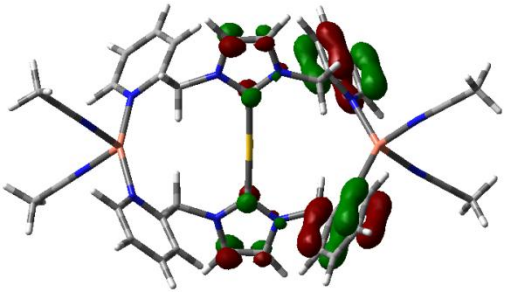

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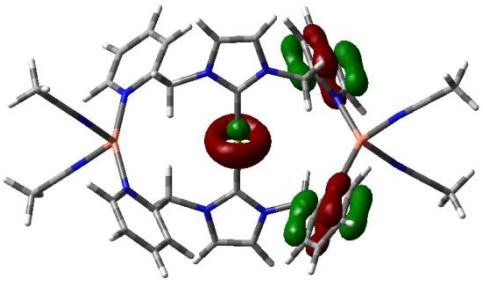

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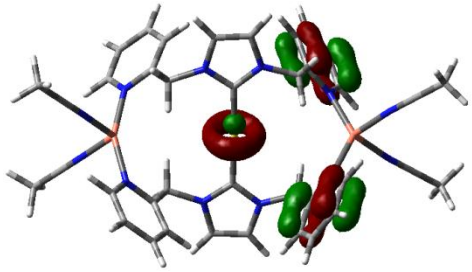

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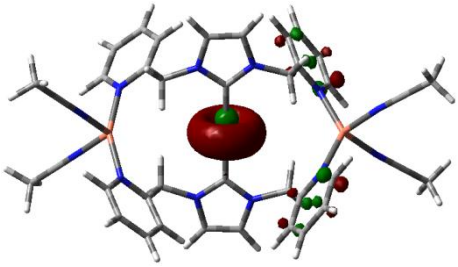

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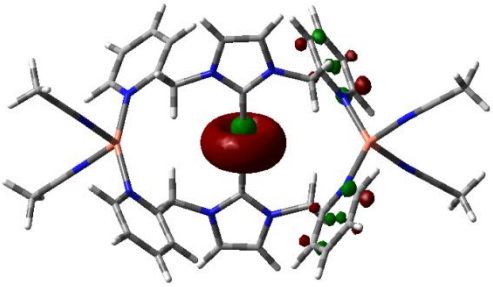

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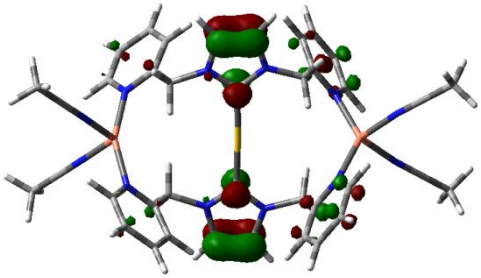

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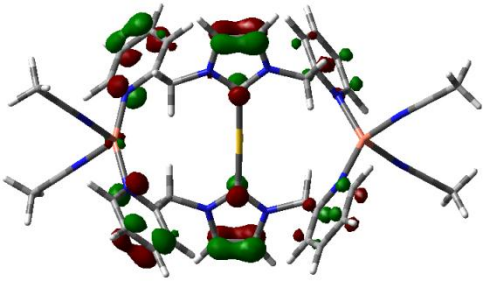

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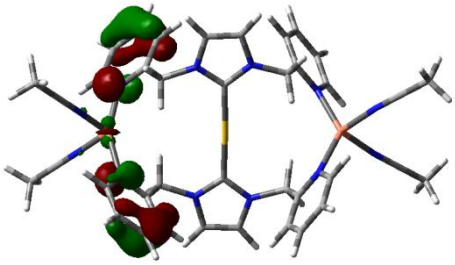

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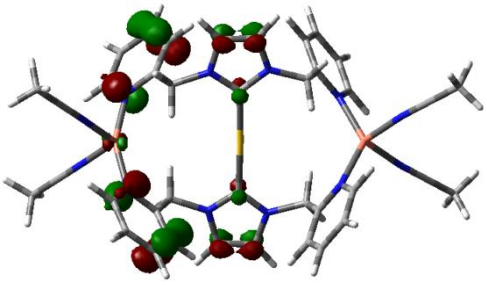

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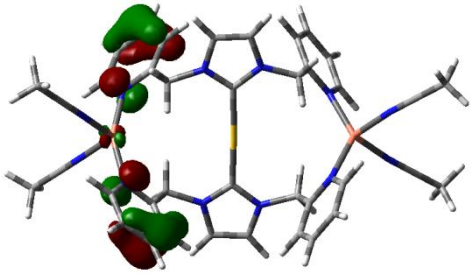

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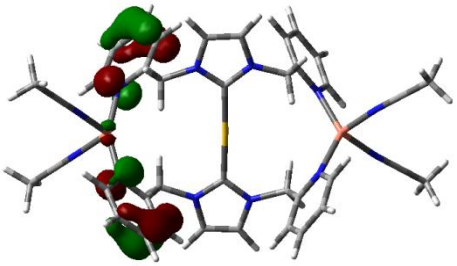

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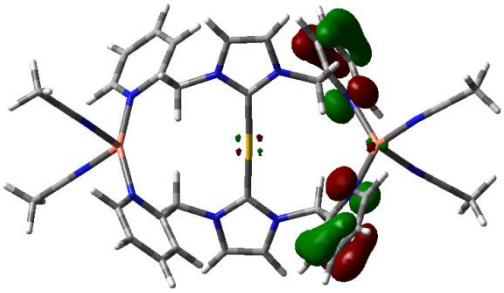

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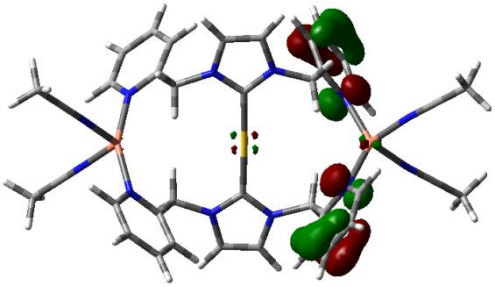

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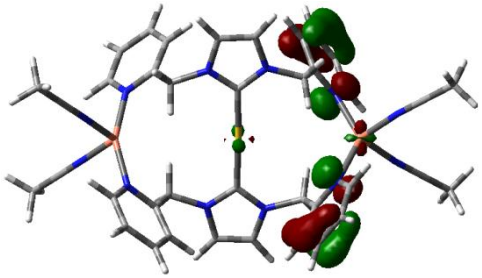

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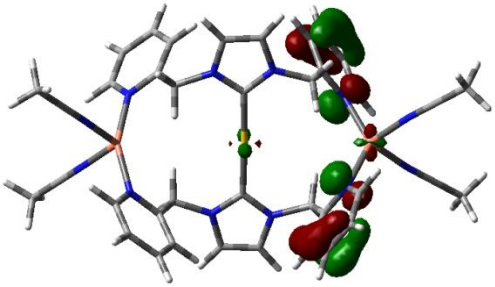

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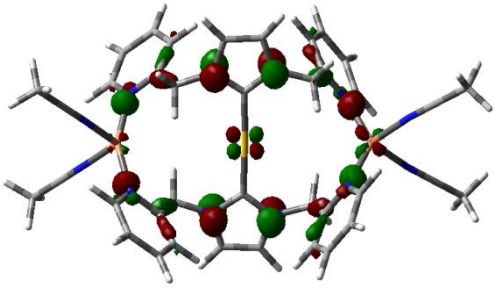

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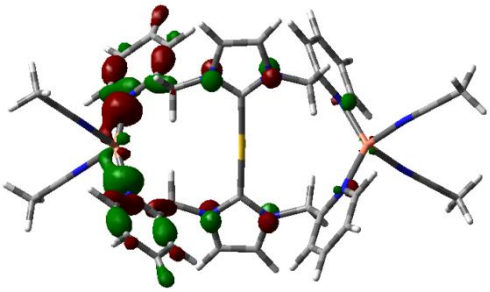

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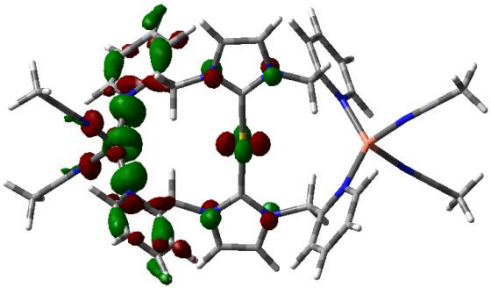

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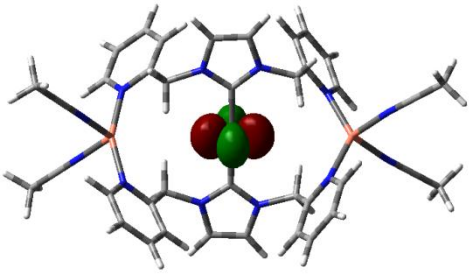

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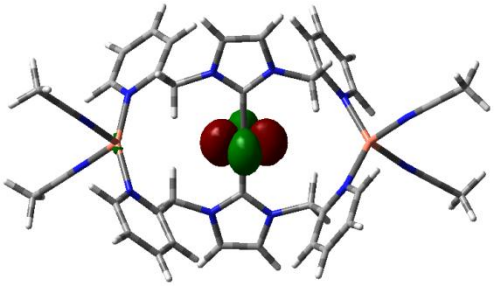

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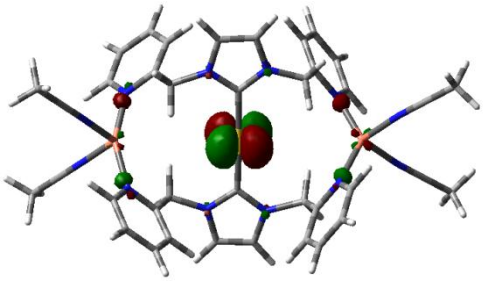

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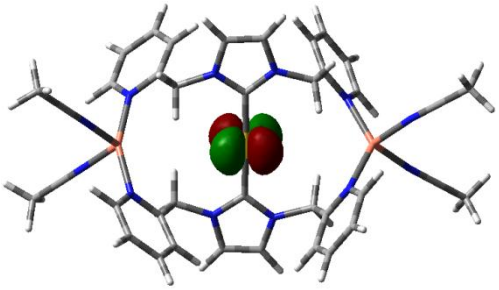

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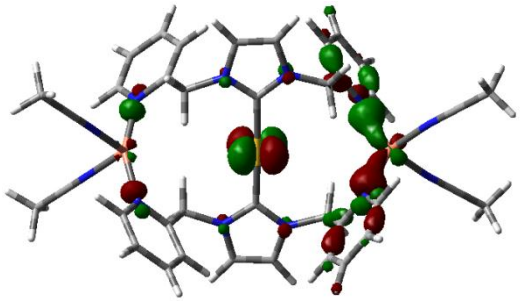

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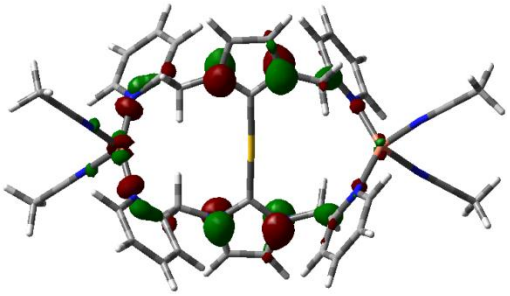

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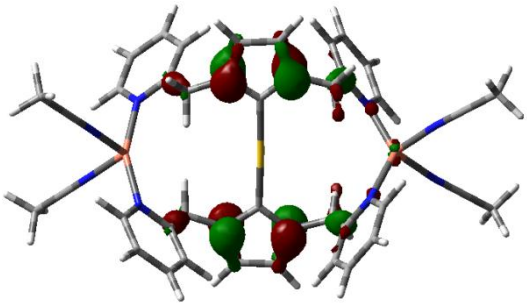

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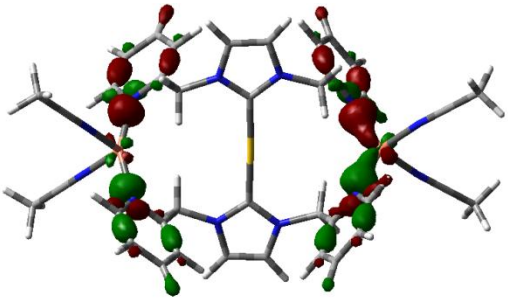

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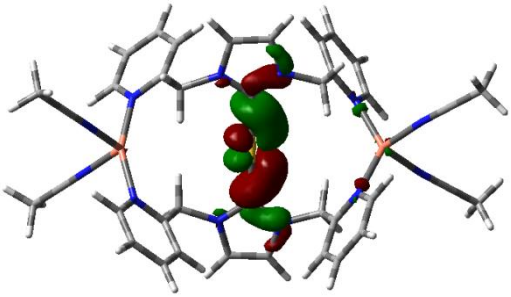

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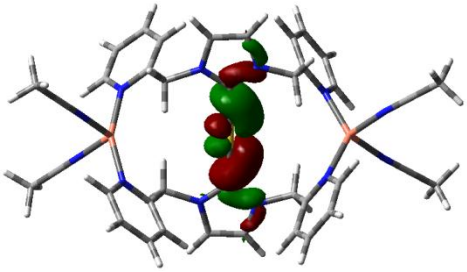

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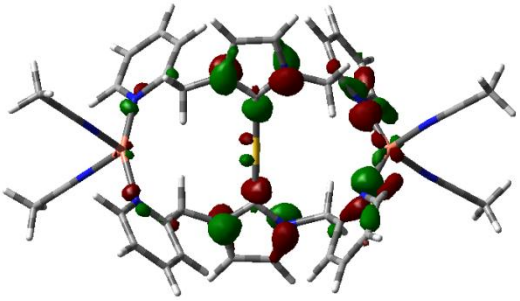

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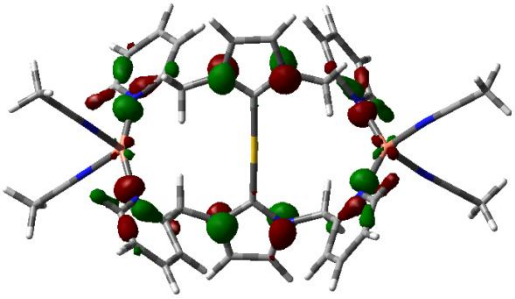

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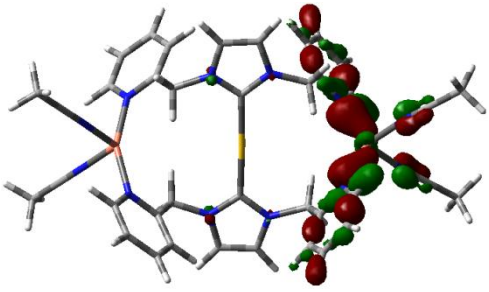

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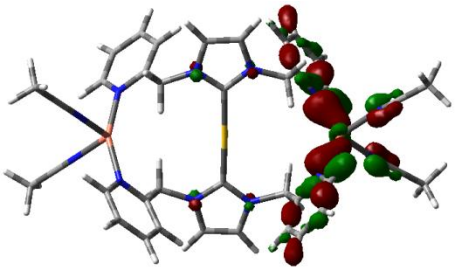

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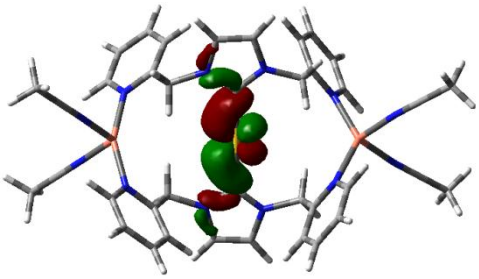

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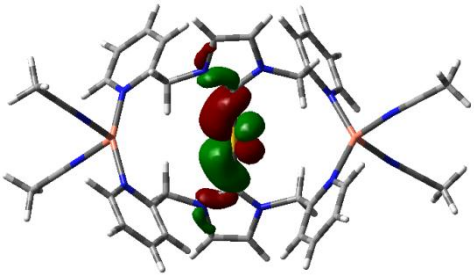

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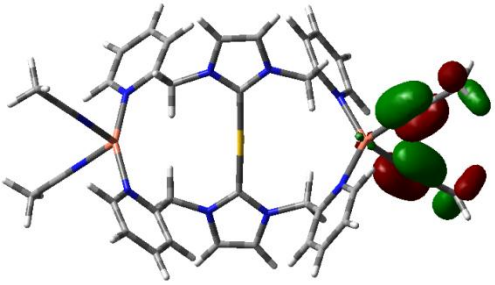

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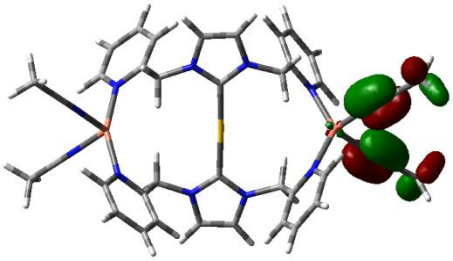

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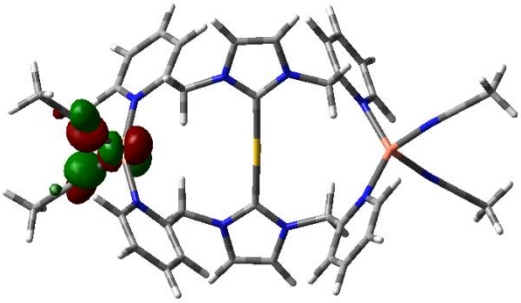

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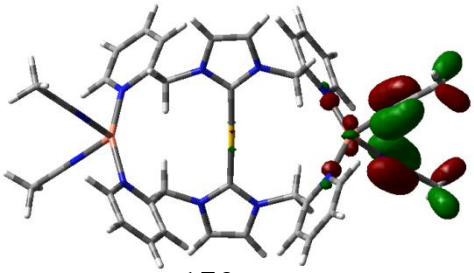

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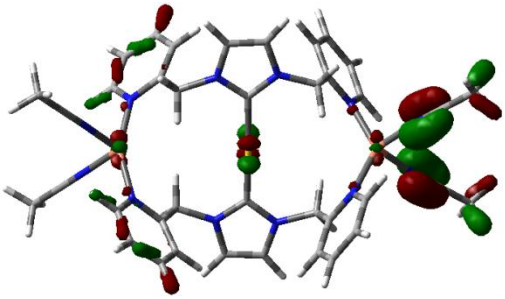

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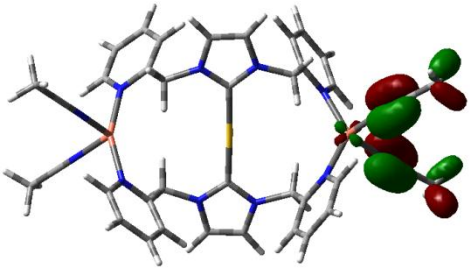

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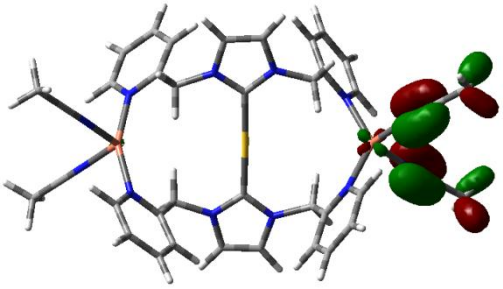

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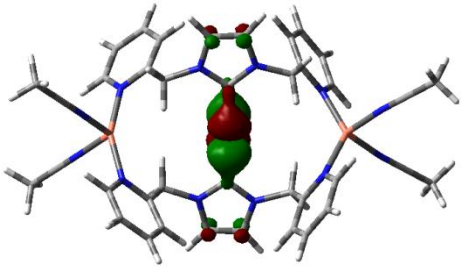

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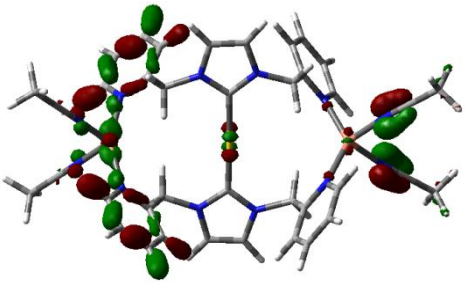

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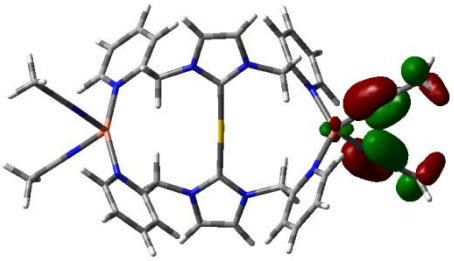

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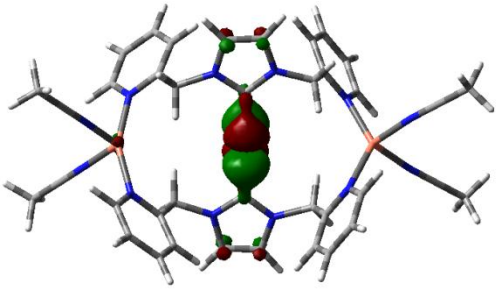

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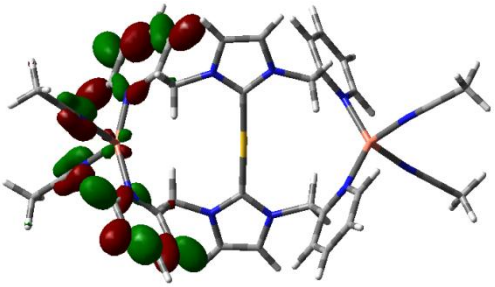

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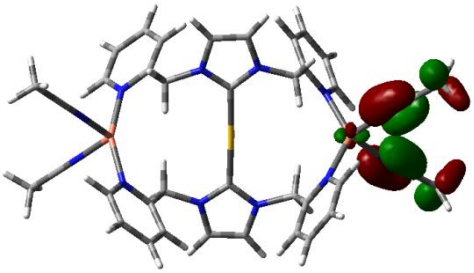

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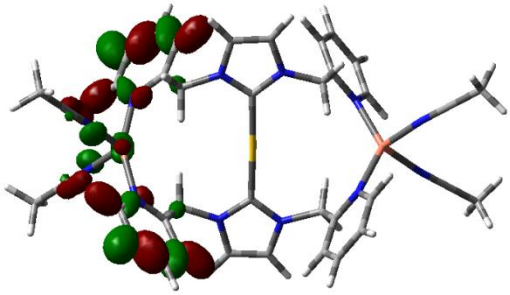

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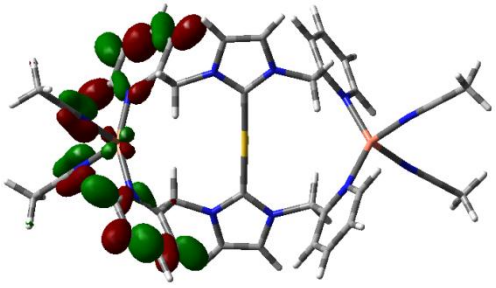

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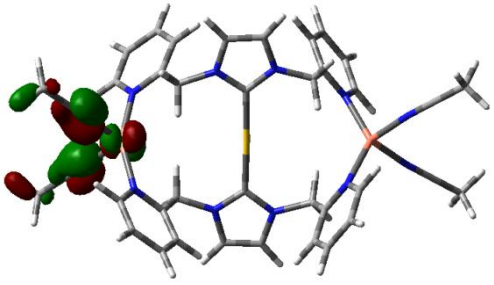

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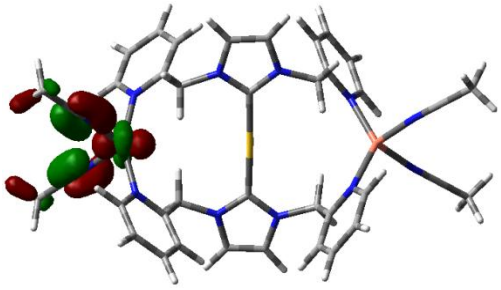

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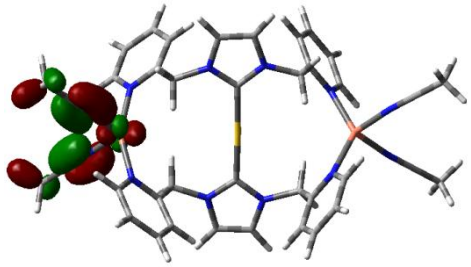

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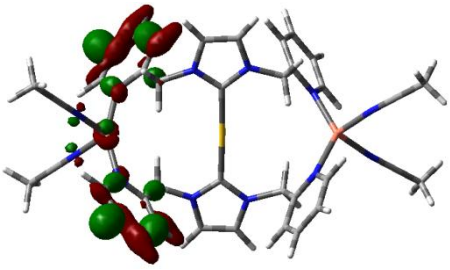

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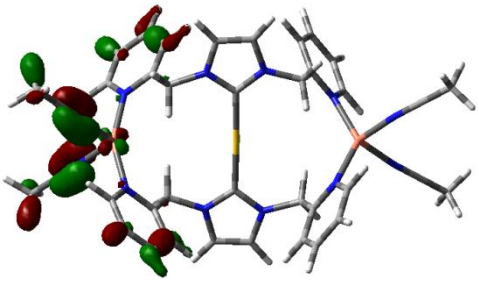

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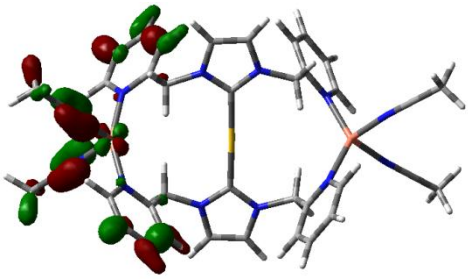

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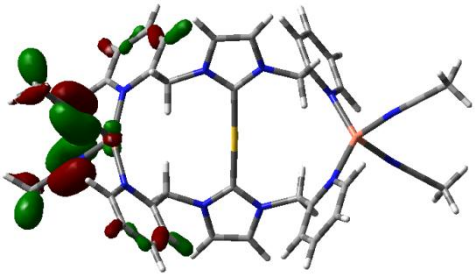

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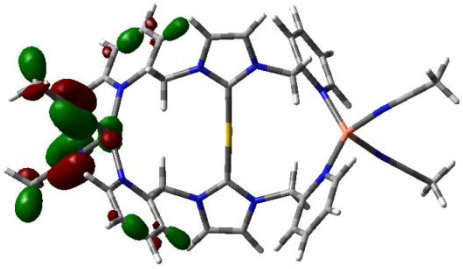

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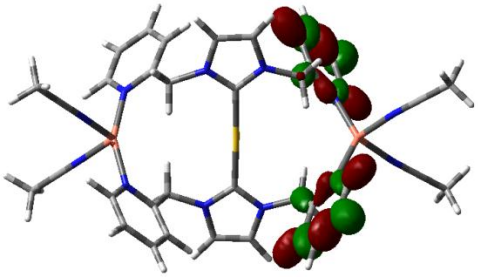

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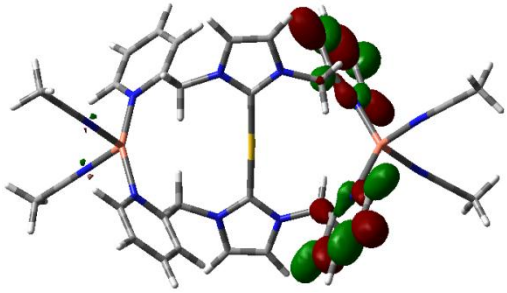

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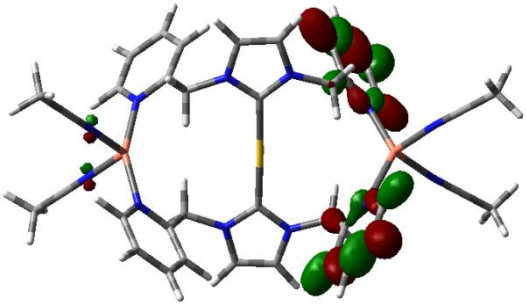

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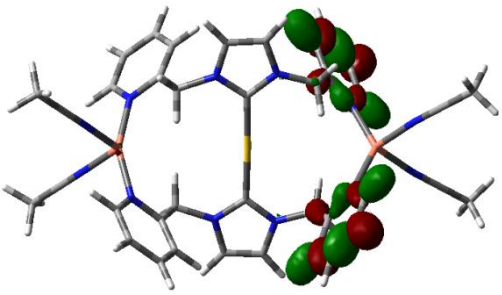

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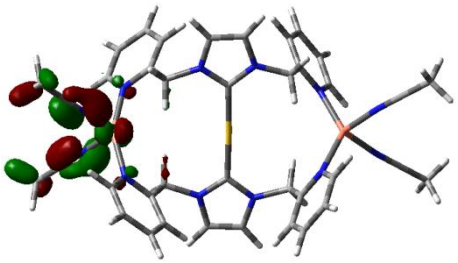

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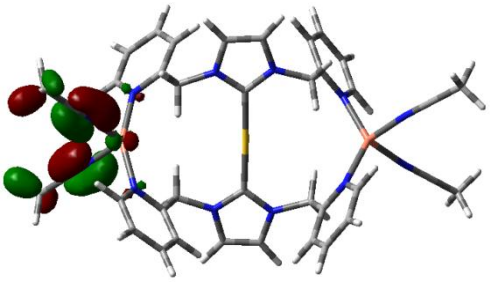

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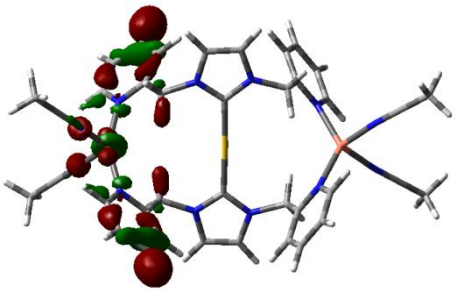

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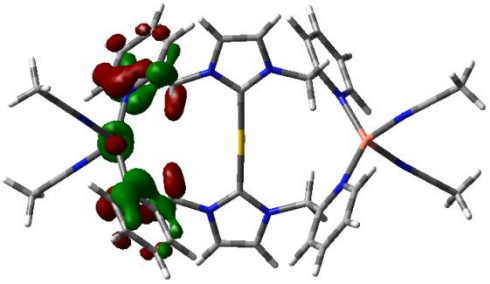

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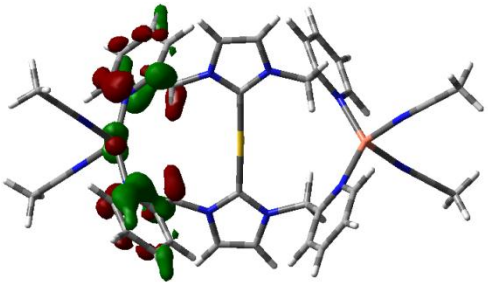

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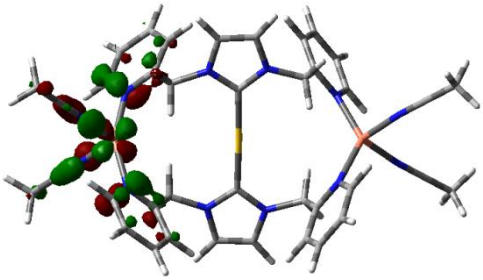

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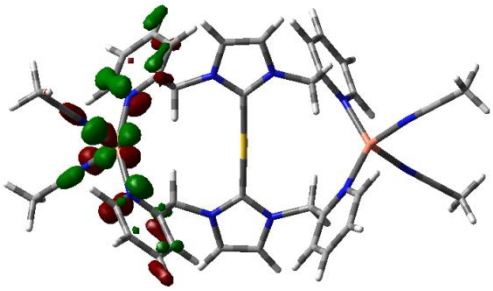

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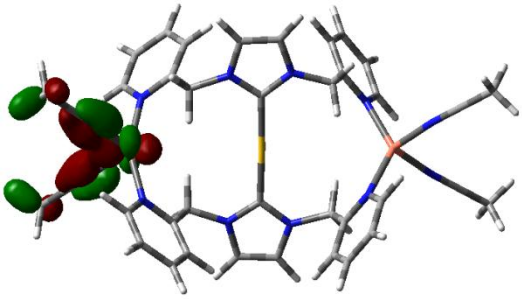

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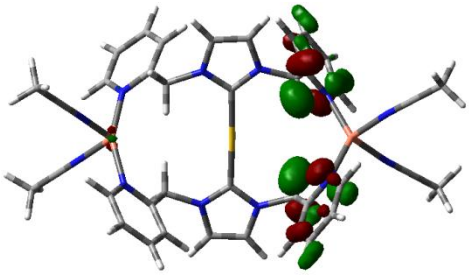

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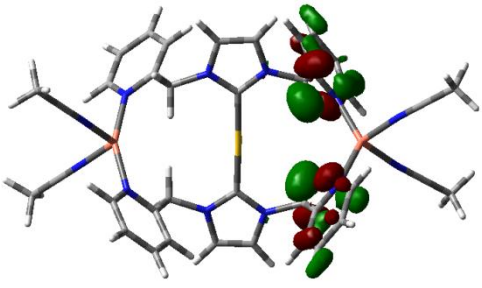

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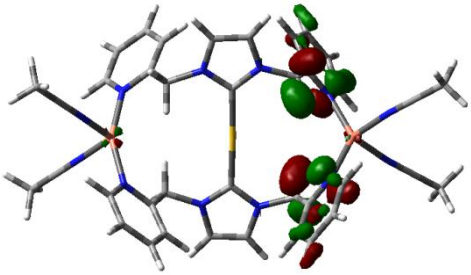

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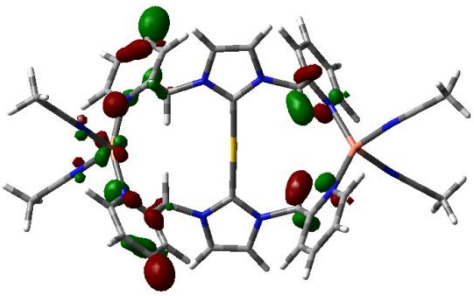

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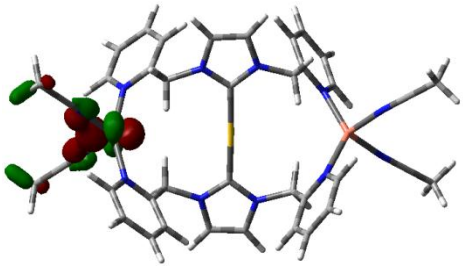

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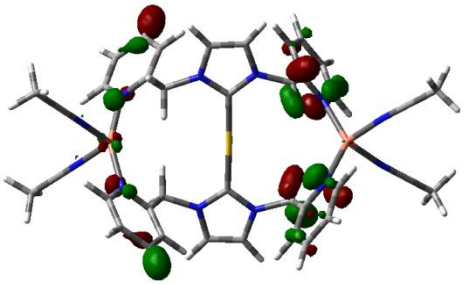

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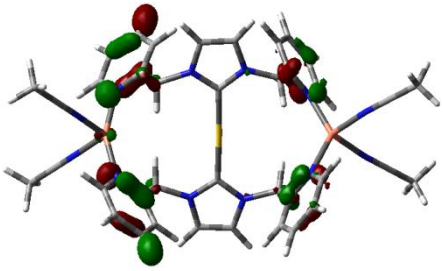

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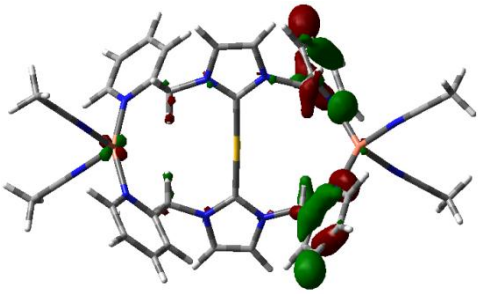

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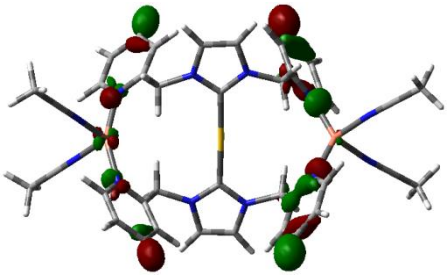

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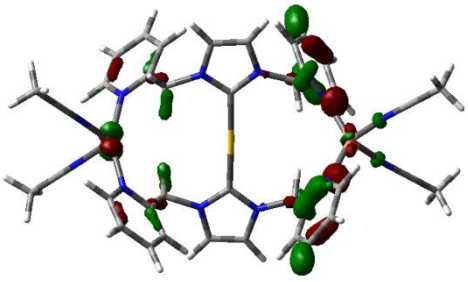

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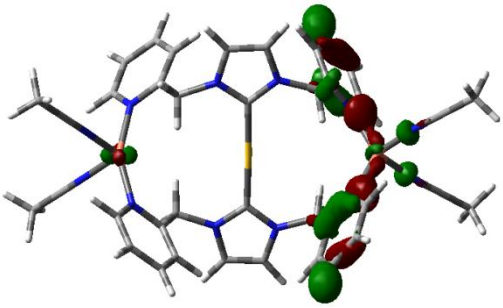

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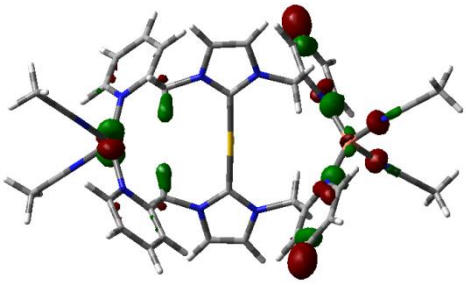
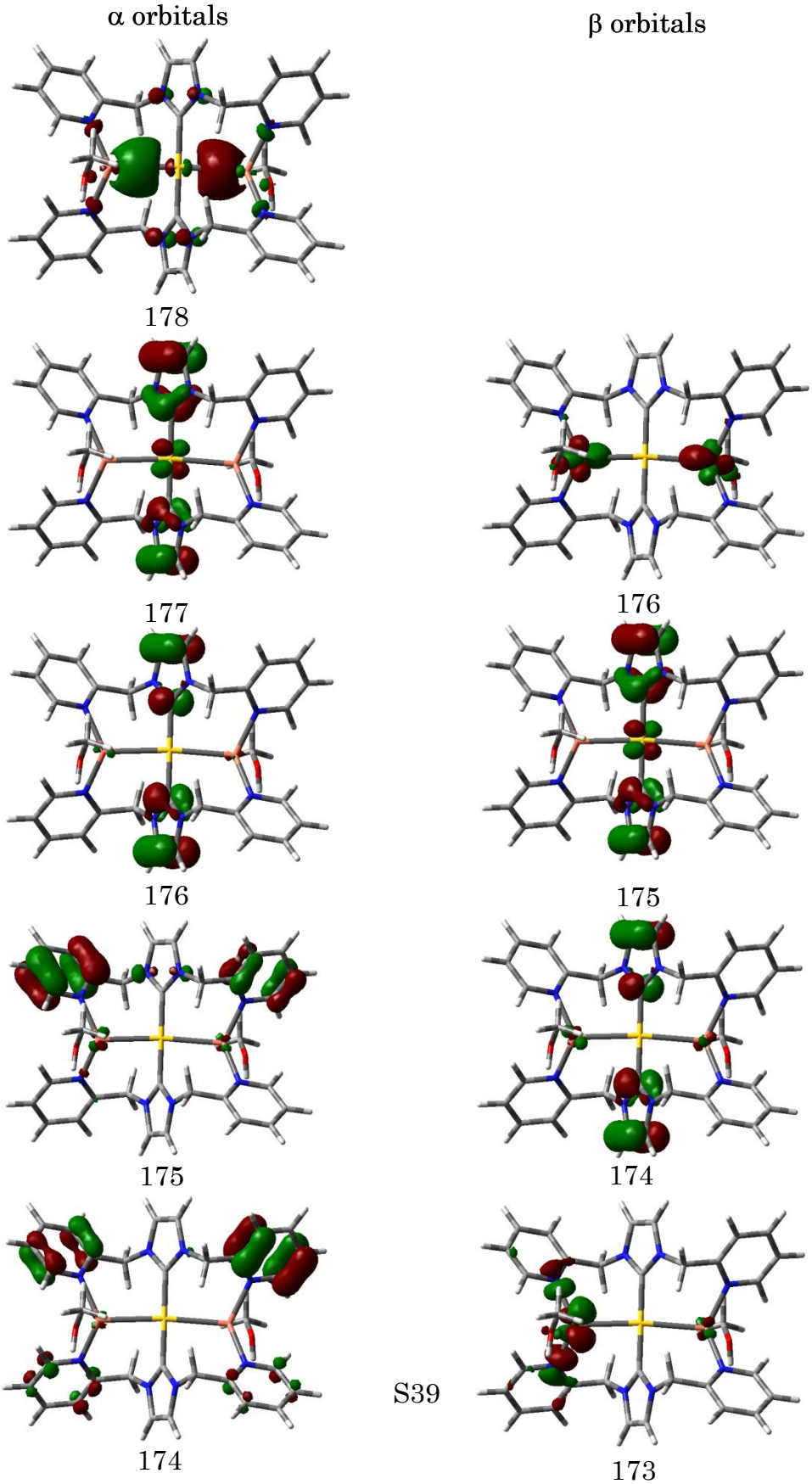
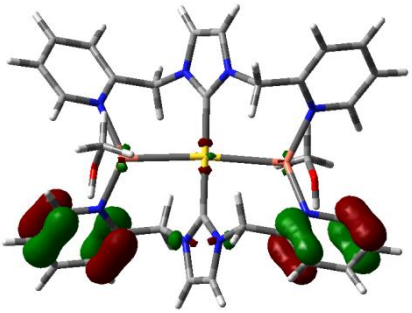


154

Figure S4. The frontier orbitals of **1** in the T_1 state

Occupied α and β spin orbitals of **2** in the T_1 state





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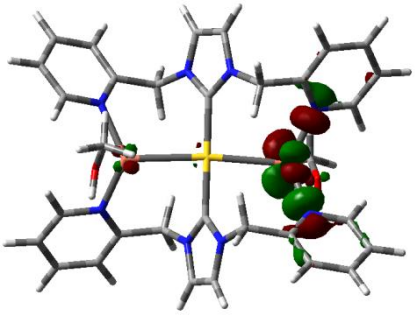

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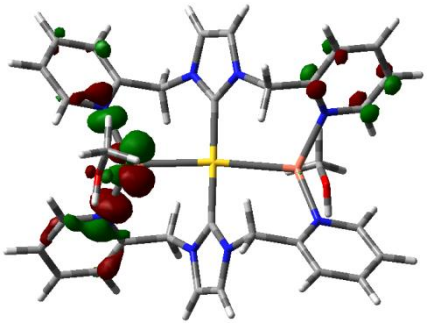

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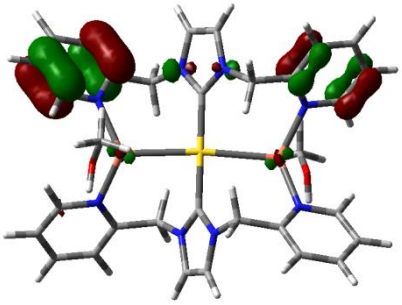

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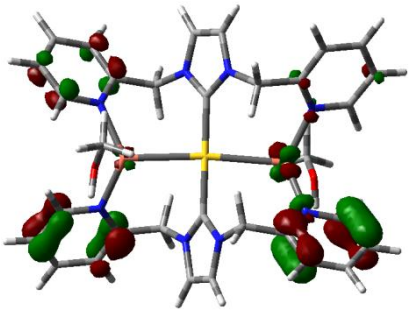

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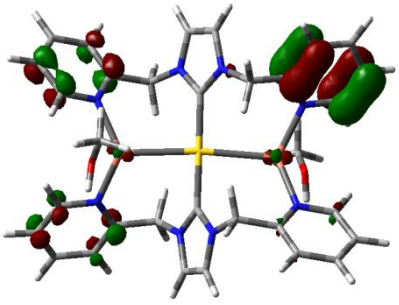

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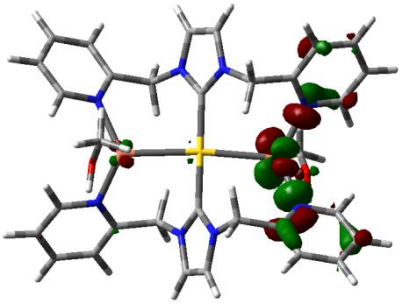

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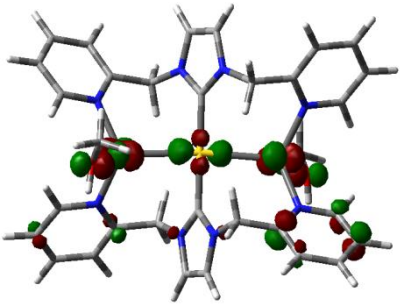

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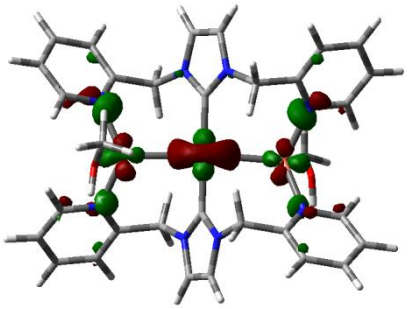

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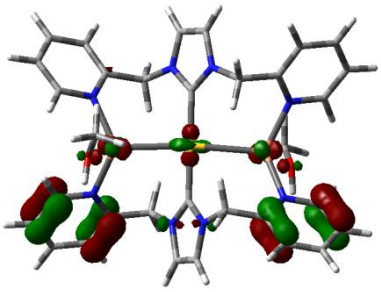

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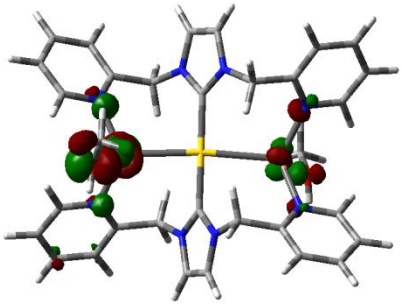

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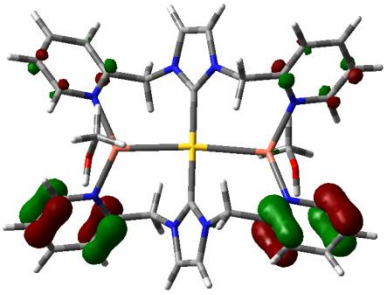

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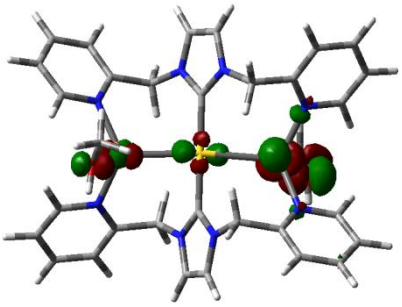

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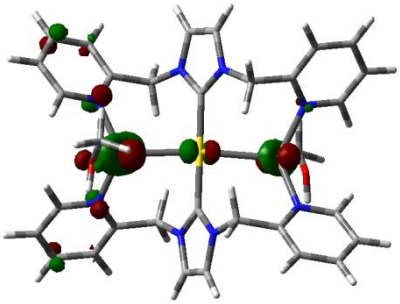

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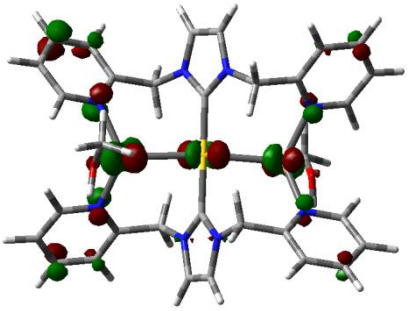

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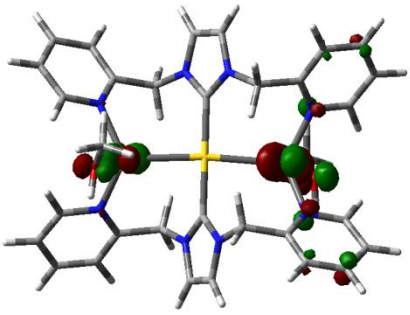

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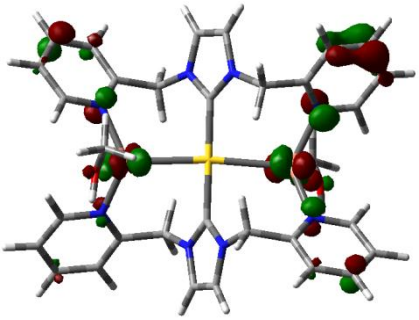

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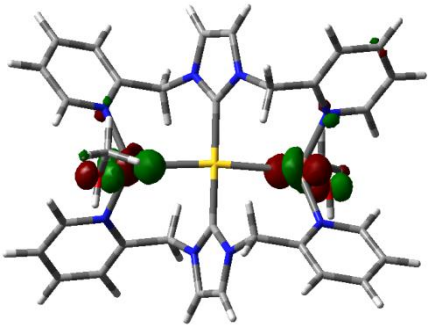

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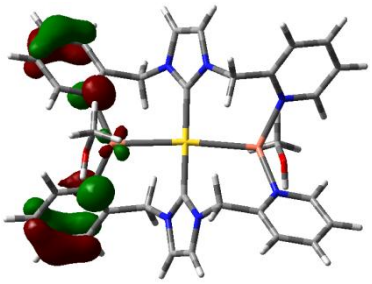

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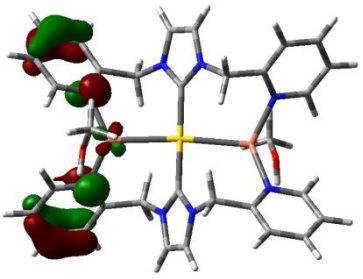

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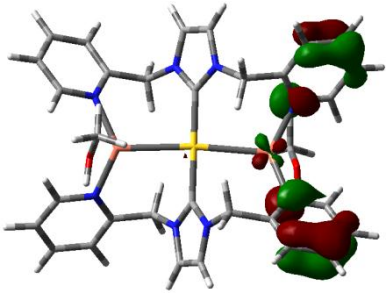

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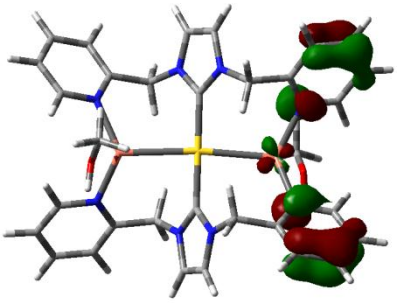

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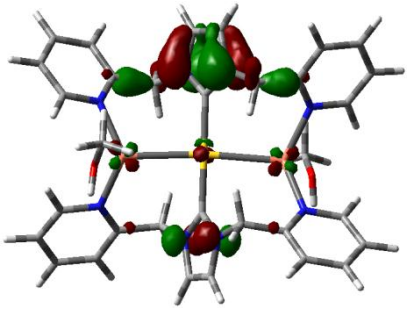

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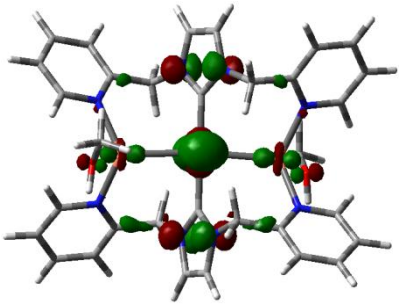

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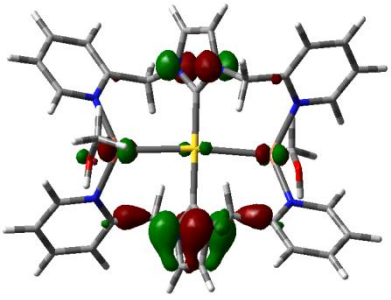

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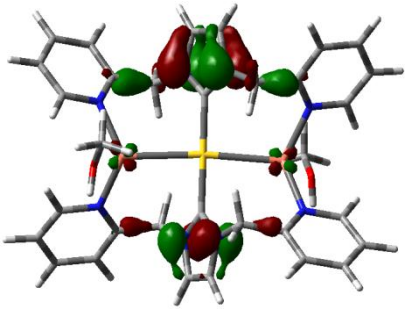

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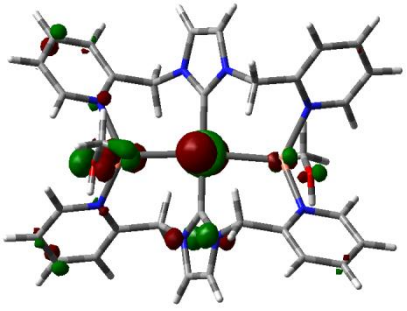

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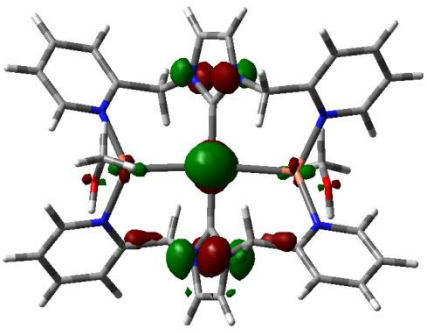

159

Figure S5. The frontier orbitals of **2** in the T_1 state