Supporting Information for

Spectroscopic and DFT Investigation of [M{HB(3,5-$^{i}Pr_2pz)_3$}(SC_6F_5)] (M = Mn, Fe, Co, Ni, Cu, and Zn) Model Complexes: Periodic Trends in Metal-thiolate Bonding

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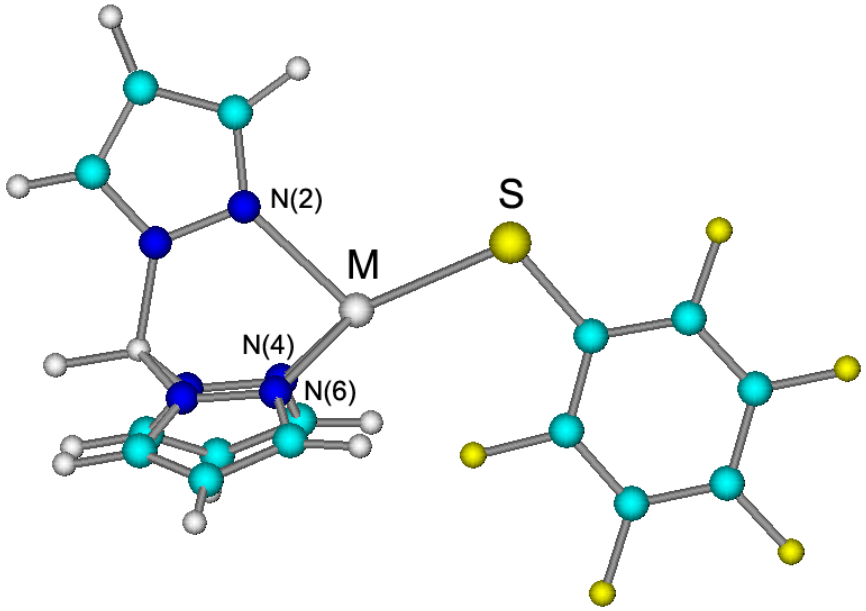
The B3LYP/6-311+G(d) optimized geometries of the [M(HB(pz)$_3$)(SC$_6$F$_5$)] complexes (the xyz atomic coordinates are given in Å)



[MnL(SC$_6$F$_5$)]

Mn	-0.550621	-0.797122	0.000000
N	-1.686097	-2.656742	0.000000
N	-0.927471	-3.788978	0.000000
N	0.732907	-1.673941	1.513934
N	1.104626	-2.962602	1.268845
N	0.732907	-1.673941	-1.513934
N	1.104626	-2.962602	-1.268845
C	-2.965500	-3.046750	0.000000
C	-3.050914	-4.443770	0.000000
C	-1.731290	-4.871415	0.000000
C	1.306704	-1.317492	2.668061
C	2.060047	-2.376129	3.187767
C	1.902134	-3.399105	2.264465
C	1.306704	-1.317492	-2.668061
C	2.060047	-2.376129	-3.187767
C	1.902134	-3.399105	-2.264465
B	0.624373	-3.720875	0.000000
H	1.152584	-0.324744	3.065135
H	2.636354	-2.395063	4.098925
H	1.152584	-0.324744	-3.065135
H	2.636354	-2.395063	-4.098925
H	1.075787	-4.829769	0.000000
H	-3.756375	-2.310595	0.000000
H	-3.940373	-5.053368	0.000000
H	2.301181	-4.401544	-2.247672
H	2.301181	-4.401544	2.247672
H	-1.312108	-5.865796	0.000000
S	-1.938428	1.153774	0.000000
C	-0.862718	2.551874	0.000000
C	-1.388893	3.853081	0.000000
C	-0.582479	4.983048	0.000000
C	0.802024	4.855454	0.000000
C	1.362407	3.584959	0.000000

C	0.532568	2.474382	0.000000
F	-2.716067	4.036827	0.000000
F	-1.132584	6.203736	0.000000
F	1.584250	5.941796	0.000000
F	2.694786	3.439309	0.000000
F	1.132173	1.253159	0.000000

[FeL(SC_6F_5)]

Fe	-0.448243	-0.789274	0.000000
N	-1.657785	-2.524912	0.000000
N	-0.976727	-3.704543	0.000000
N	0.718490	-1.665165	1.519932
N	1.073575	-2.957337	1.270077
N	0.718490	-1.665165	-1.519932
N	1.073575	-2.957337	-1.270077
C	-2.960245	-2.828125	0.000000
C	-3.137111	-4.216777	0.000000
C	-1.848380	-4.732242	0.000000
C	1.305493	-1.312907	2.668119
C	2.053155	-2.379859	3.179924
C	1.877450	-3.400759	2.257840
C	1.305493	-1.312907	-2.668119
C	2.053155	-2.379859	-3.179924
C	1.877450	-3.400759	-2.257840
B	0.572350	-3.704789	0.000000
H	1.163240	-0.319203	3.066812
H	2.635529	-2.405197	4.087018
H	1.163240	-0.319203	-3.066812
H	2.635529	-2.405197	-4.087018
H	0.989576	-4.826721	0.000000
H	-3.698422	-2.039433	0.000000
H	-4.064831	-4.766467	0.000000
H	2.266137	-4.407152	-2.237174
H	2.266137	-4.407152	2.237174
H	-1.496619	-5.752530	0.000000
S	-1.851919	1.040386	0.000000
C	-0.825453	2.480896	0.000000
C	-1.390762	3.764233	0.000000
C	-0.617497	4.917519	0.000000
C	0.770089	4.829578	0.000000
C	1.368505	3.576138	0.000000
C	0.570714	2.442617	0.000000
F	-2.722943	3.908514	0.000000
F	-1.202065	6.121933	0.000000
F	1.519782	5.938272	0.000000
F	2.704483	3.470305	0.000000
F	1.201198	1.237378	0.000000

[CoL(SC_6F_5)]

Co	-0.467114	-0.835205	0.000000
N	-1.660116	-2.528281	0.000000
N	-0.945858	-3.688050	0.000000
N	0.736804	-1.599546	1.487314
N	1.095381	-2.896021	1.266203
N	0.736804	-1.599546	-1.487314
N	1.095381	-2.896021	-1.266203
C	-2.952676	-2.862648	0.000000
C	-3.092842	-4.256977	0.000000
C	-1.792749	-4.738598	0.000000
C	1.315798	-1.219654	2.628833
C	2.062406	-2.274943	3.168064
C	1.894513	-3.316481	2.268335
C	1.315798	-1.219654	-2.628833
C	2.062406	-2.274943	-3.168064
C	1.894513	-3.316481	-2.268335
B	0.606721	-3.658742	0.000000

H	1.169004	-0.217488	3.003345
H	2.640570	-2.278468	4.078184
H	1.169004	-0.217488	-3.003345
H	2.640570	-2.278468	-4.078184
H	1.041571	-4.773444	0.000000
H	-3.711290	-2.093657	0.000000
H	-4.006481	-4.829666	0.000000
H	2.286953	-4.321616	-2.270988
H	2.286953	-4.321616	2.270988
H	-1.413786	-5.748956	0.000000
S	-1.831753	0.984963	0.000000
C	-0.822473	2.433960	0.000000
C	-1.407680	3.708295	0.000000
C	-0.652809	4.873427	0.000000
C	0.735780	4.806056	0.000000
C	1.352725	3.561674	0.000000
C	0.574655	2.413813	0.000000
F	-2.742338	3.830405	0.000000
F	-1.256097	6.068527	0.000000
F	1.468750	5.925721	0.000000
F	2.690180	3.476853	0.000000
F	1.222892	1.222592	0.000000

[NiL(SC_6F_5)]

Ni	-0.348922	-0.766098	0.000000
N	-1.625444	-2.359575	0.000000
N	-1.041019	-3.586734	0.000000
N	0.783297	-1.659049	1.435990
N	1.050744	-2.978513	1.255980
N	0.783297	-1.659049	-1.435990
N	1.050744	-2.978513	-1.255980
C	-2.946760	-2.549736	0.000000
C	-3.236284	-3.920877	0.000000
C	-1.995397	-4.540029	0.000000
C	1.354610	-1.292851	2.586376
C	2.006933	-2.386475	3.170420
C	1.786153	-3.435150	2.289804
C	1.354610	-1.292851	-2.586376
C	2.006933	-2.386475	-3.170420
C	1.786153	-3.435150	-2.289804
B	0.505594	-3.709249	0.000000
H	1.271100	-0.274181	2.935000
H	2.558906	-2.409618	4.096399
H	1.271100	-0.274181	-2.935000
H	2.558906	-2.409618	-4.096399
H	0.839033	-4.858621	0.000000
H	-3.617233	-1.702995	0.000000
H	-4.206532	-4.391314	0.000000
H	2.099398	-4.467066	-2.327311
H	2.099398	-4.467066	2.327311
H	-1.726849	-5.585183	0.000000
S	-1.815812	0.968626	0.000000
C	-0.808983	2.417776	0.000000
C	-1.382408	3.697508	0.000000
C	-0.614366	4.854358	0.000000
C	0.773777	4.772817	0.000000
C	1.379943	3.522605	0.000000
C	0.587450	2.385946	0.000000
F	-2.714663	3.833645	0.000000
F	-1.204196	6.055567	0.000000
F	1.517232	5.884740	0.000000
F	2.715816	3.424251	0.000000
F	1.221600	1.181836	0.000000

[CuL(SC_6F_5)]

Cu	-0.324083	-0.809917	0.000000
N	-1.684349	-2.577237	0.000000

N	-0.993949	-3.749038	0.000000
N	0.781502	-1.681457	1.442125
N	1.067681	-2.995892	1.257737
N	0.781502	-1.681457	-1.442125
N	1.067681	-2.995892	-1.257737
C	-2.978366	-2.898388	0.000000
C	-3.145134	-4.292943	0.000000
C	-1.853575	-4.792789	0.000000
C	1.335598	-1.311908	2.599891
C	1.993527	-2.399914	3.187307
C	1.796629	-3.446705	2.298492
C	1.335598	-1.311908	-2.599891
C	1.993527	-2.399914	-3.187307
C	1.796629	-3.446705	-2.298492
B	0.551197	-3.751710	0.000000
H	1.237536	-0.294936	2.949236
H	2.535380	-2.420603	4.119383
H	1.237536	-0.294936	-2.949236
H	2.535380	-2.420603	-4.119383
H	0.966178	-4.875438	0.000000
H	-3.728237	-2.120091	0.000000
H	-4.067432	-4.852274	0.000000
H	2.122467	-4.474687	-2.334520
H	2.122467	-4.474687	2.334520
H	-1.487999	-5.808290	0.000000
S	-1.618957	0.973434	0.000000
C	-0.717441	2.484578	0.000000
C	-1.421682	3.701608	0.000000
C	-0.779424	4.931091	0.000000
C	0.610025	4.985789	0.000000
C	1.342252	3.804270	0.000000
C	0.681931	2.584337	0.000000
F	-2.758225	3.700846	0.000000
F	-1.486012	6.065835	0.000000
F	1.236071	6.163612	0.000000
F	2.679141	3.852272	0.000000
F	1.439186	1.476501	0.000000

$[ZnL(SC_6F_5)]$

Zn	-0.525210	-0.826508	0.000000
N	-1.628963	-2.610650	0.000000
N	-0.863399	-3.736170	0.000000
N	0.718168	-1.581138	1.483718
N	1.139311	-2.857113	1.264390
N	0.718168	-1.581138	-1.483718
N	1.139311	-2.857113	-1.264390
C	-2.905274	-3.003574	0.000000
C	-2.982511	-4.402088	0.000000
C	-1.661096	-4.823487	0.000000
C	1.261892	-1.179179	2.634968
C	2.048833	-2.200181	3.181734
C	1.941056	-3.245494	2.276512
C	1.261892	-1.179179	-2.634968
C	2.048833	-2.200181	-3.181734
C	1.941056	-3.245494	-2.276512
B	0.686836	-3.639063	0.000000
H	1.064585	-0.185753	3.009807
H	2.614762	-2.180163	4.099304
H	1.064585	-0.185753	-3.009807
H	2.614762	-2.180163	-4.099304
H	1.168295	-4.734806	0.000000
H	-3.698732	-2.270454	0.000000
H	-3.868928	-5.016050	0.000000
H	2.377722	-4.232226	-2.282523
H	2.377722	-4.232226	2.282523
H	-1.236472	-5.815545	0.000000
S	-1.858841	1.020660	0.000000
C	-0.816037	2.447871	0.000000

```
C    -1.403648             3.722149      0.000000
C    -0.654404             4.890339      0.000000
C     0.734198             4.829006      0.000000
C     1.353346             3.586675      0.000000
C     0.581679             2.433296      0.000000
F    -2.739073             3.840174      0.000000
F    -1.263955             6.082311      0.000000
F     1.463348             5.951337      0.000000
F     2.691140             3.505375      0.000000
F     1.240564             1.251195      0.000000
```

Calculated electronic energy (E, a.u.), HOMO/LUMO energies, metal-ligand distances (Å), atomic charges, q(NPA) and spin densities, s(MPA) and s(NPA), at the B3LYP/6-311+G(d) levels.

[MnL(SC_6F_5)]

```
E= -2979.9140267 a.u.
 Alpha HOMO= -5.803 eV, LUMO= -1.001 eV, Gap= 4.802 eV
 Beta  HOMO= -6.049 eV, LUMO= -1.642 eV, Gap= 4.407 eV
--- GEOMETRY ---
 M-S    M-N(ax) M-N(eq)
 2.394  2.179   2.170

        Mn(1)  N(2)   N(4)   N(6)   S(28)  F(35)  F(39)  SC6F5
q(NPA): 1.369 -0.449 -0.449 -0.449 -0.356 -0.321 -0.349 -0.678
s(MPA): 4.880 -0.001  0.006  0.006 -0.001 -0.001 -0.009  0.055
s(NPA): 4.620  0.056  0.049  0.049  0.088  0.001  0.016  0.133
```

[FeL(SC_6F_5)]

```
E= -3092.6035539 a.u.
 Alpha HOMO= -5.920 eV, LUMO= -1.002 eV, Gap= 4.917 eV
 Beta  HOMO= -6.039 eV, LUMO= -2.351 eV, Gap= 3.688 eV
--- GEOMETRY ---
 M-S    M-N(ax)  M-N(eq)
 2.306  2.116    2.107

        Fe(1)  N(2)   N(4)   N(6)   S(28)  F(35)  F(39)  SC6F5
q(NPA): 1.300 -0.433 -0.440 -0.440 -0.320 -0.321 -0.348 -0.644
s(MPA): 3.743  0.051  0.037  0.037  0.061  0.000 -0.004  0.112
s(NPA): 3.578  0.074  0.065  0.065  0.129  0.001  0.014  0.164
```

[CoL(SC_6F_5)]

```
E= -3211.6515757 a.u.
Alpha HOMO= -5.966 eV, LUMO= -0.989 eV, Gap= 4.977 eV
Beta  HOMO= -6.031 eV, LUMO= -2.816 eV, Gap= 3.215 eV
--- GEOMETRY ---
 M-S    M-N(ax)  M-N(eq)
 2.275  2.071    2.061

        Co(1)  N(2)   N(4)   N(6)   S(28)  F(35)  F(39)  SC6F5
q(NPA): 1.271 -0.429 -0.432 -0.432 -0.307 -0.321 -0.343 -0.623
s(MPA): 2.684  0.073  0.056  0.056  0.119  0.000  0.000  0.132
s(NPA): 2.575  0.079  0.071  0.071  0.157  0.001  0.009  0.186
```

[NiL(SC_6F_5)]

```
E= -3337.1880487 a.u.
 Alpha HOMO= -6.087 eV, LUMO= -1.065 eV, Gap= 5.022 eV
 Beta  HOMO= -6.220 eV, LUMO= -2.842 eV, Gap= 3.378 eV
--- GEOMETRY ---
 M-S    M-N(ax)  M-N(eq)
 2.272  2.042    2.035

        Ni(1)  N(2)   N(4)   N(6)   S(28)  F(35)  F(39)  SC6F5
q(NPA): 1.236 -0.405 -0.417 -0.417 -0.324 -0.320 -0.346 -0.634
s(MPA): 1.569  0.114  0.091  0.091  0.100  0.001 -0.001  0.167
s(NPA): 1.571  0.111  0.082  0.082  0.121  0.001  0.012  0.159
```

[CuL(SC_6F_5)]

```
E= -3469.3462528 a.u.
Alpha HOMO= -6.624 eV, LUMO= -1.230 eV, Gap= 5.394 eV
Beta  HOMO= -6.678 eV, LUMO= -4.296 eV , Gap= 2.382 eV
--- GEOMETRY ---
 M-S    M-N(ax) M-N(eq)
 2.204  2.230   2.015

        Cu(1)  N(2)   N(4)   N(6)   S(28)  F(35)  F(39)  SC6F5
q(NPA): 1.127 -0.425 -0.415 -0.415 -0.189 -0.316 -0.325 -0.432
s(MPA): 0.439 -0.001  0.076  0.076  0.292  0.002  0.005  0.408
s(NPA): 0.470 -0.001  0.075  0.075  0.307  0.004  0.005  0.384
```

[ZnL(SC_6F_5)]

```
E= -3608.2315374 a.u.
 HOMO= -6.041 eV, LUMO= -0.999 eV, Gap= 5.042 eV
--- GEOMETRY ---
 M-S    M-N(ax) M-N(eq)
 2.278  2.098   2.078

        Zn(1)  N(2)   N(4)   N(6)   S(28)  F(35)  F(39) SC6F5
q(NPA): 1.513 -0.480 -0.478 -0.478 -0.404 -0.322 -0.343 -0.724
```

The B3LYP/6-311+G(d) optimized geometries of the [M($HB(pz)_3$)F] complexes (the xyz atomic coordinates are given in Å)

[Mn(L)F]

```
Mn    0.000869             1.615515      0.000000
N    -1.749483             0.309675      0.000000
N    -1.465598            -1.023246      0.000000
N     0.876556             0.308754      1.514619
N     0.732422            -1.024105      1.268693
N     0.876556             0.308754     -1.514619
N     0.732422            -1.024105     -1.268693
C    -3.081634             0.422364      0.000000
C    -3.680594            -0.843346      0.000000
C    -2.614163            -1.730160      0.000000
C     1.542051             0.420191      2.668722
C     1.838987            -0.845954      3.187697
C     1.304609            -1.731861      2.263957
C     1.542051             0.420191     -2.668722
C     1.838987            -0.845954     -3.187697
C     1.304609            -1.731861     -2.263957
B    -0.000819            -1.542057      0.000000
```

H	1.773122	1.397980	3.066207
H	2.364417	-1.082925	4.099094
H	1.773122	1.397980	-3.066207
H	2.364417	-1.082925	-4.099094
H	-0.002209	-2.739910	0.000000
H	-3.540361	1.400613	0.000000
H	-4.732804	-1.079466	0.000000
H	1.292782	-2.810751	-2.246780
H	1.292782	-2.810751	2.246780
H	-2.594203	-2.809078	0.000000
F	0.000197	3.483323	0.000000

[Fe(L)F]

Fe	-1.553025	0.137403	0.000000
N	-0.106230	1.724635	0.000000
N	1.193069	1.320790	0.000000
N	-0.404286	-0.850430	1.480695
N	0.940731	-0.856007	1.264208
N	-0.404286	-0.850430	-1.480695
N	0.940731	-0.856007	-1.264208
C	-0.100018	3.058546	0.000000
C	1.217968	3.541029	0.000000
C	2.005047	2.401385	0.000000
C	-0.617388	-1.497772	2.631035
C	0.596114	-1.931639	3.177907
C	1.557034	-1.502226	2.273904
C	-0.617388	-1.497772	-2.631035
C	0.596114	-1.931639	-3.177907
C	1.557034	-1.502226	-2.273904
B	1.552575	-0.185166	0.000000
H	-1.623417	-1.615981	3.006636
H	0.752249	-2.477639	4.094584
H	-1.623417	-1.615981	-3.006636
H	0.752249	-2.477639	-4.094584
H	2.741543	-0.327537	0.000000
H	-1.033698	3.601982	0.000000
H	1.547191	4.567998	0.000000
H	2.630436	-1.612486	-2.279896
H	2.630436	-1.612486	2.279896
H	3.077501	2.282193	0.000000
F	-3.280055	0.709663	0.000000

[Co(L)F]

Co	1.465439	0.006016	0.000000
N	0.305861	1.716344	0.000000
N	-1.031780	1.458206	0.000000
N	0.315377	-0.856296	1.484832
N	-1.023728	-0.734297	1.265412
N	0.315377	-0.856296	-1.484832
N	-1.023728	-0.734297	-1.265412
C	0.451707	3.042870	0.000000
C	-0.802990	3.668184	0.000000
C	-1.713644	2.622975	0.000000
C	0.468149	-1.520906	2.631972
C	-0.783148	-1.841663	3.176510
C	-1.699310	-1.322347	2.275013
C	0.468149	-1.520906	-2.631972
C	-0.783148	-1.841663	-3.176510
C	-1.699310	-1.322347	-2.275013
B	-1.560349	-0.004774	0.000000
H	1.459337	-1.732923	3.005190
H	-0.989713	-2.373311	4.091629
H	1.459337	-1.732923	-3.005190
H	-0.989713	-2.373311	-4.091629
H	-2.757234	-0.008593	0.000000
H	1.440754	3.476960	0.000000
H	-1.015219	4.725411	0.000000
H	-2.778294	-1.330058	-2.281263
H	-2.778294	-1.330058	2.281263

H	-2.792675	2.626560	0.000000
F	3.281803	0.019439	0.000000

[Ni(L)F]

Ni	1.441576	0.120960	0.000000
N	0.126449	1.660903	0.000000
N	-1.191773	1.333252	0.000000
N	0.352775	-0.821934	1.432403
N	-0.993986	-0.836038	1.255767
N	0.352775	-0.821934	-1.432403
N	-0.993986	-0.836038	-1.255767
C	0.207092	2.993054	0.000000
C	-1.078931	3.551130	0.000000
C	-1.934536	2.459328	0.000000
C	0.609509	-1.456478	2.578998
C	-0.585875	-1.895854	3.163897
C	-1.577271	-1.478305	2.288119
C	0.609509	-1.456478	-2.578998
C	-0.585875	-1.895854	-3.163897
C	-1.577271	-1.478305	-2.288119
B	-1.609499	-0.161661	0.000000
H	1.627896	-1.563198	2.922766
H	-0.709771	-2.437306	4.088127
H	1.627896	-1.563198	-2.922766
H	-0.709771	-2.437306	-4.088127
H	-2.801458	-0.270232	0.000000
H	1.173509	3.475221	0.000000
H	-1.345831	4.595897	0.000000
H	-2.649556	-1.592228	-2.328435
H	-2.649556	-1.592228	2.328435
H	-3.012310	2.406124	0.000000
F	3.227605	0.510999	0.000000

[Cu(L)F]

Cu	1.419324	-0.400186	0.000000
N	0.534559	1.661732	0.000000
N	-0.825736	1.641659	0.000000
N	0.132867	-0.916716	1.419608
N	-1.156434	-0.526927	1.254528
N	0.132867	-0.916716	-1.419608
N	-1.156434	-0.526927	-1.254528
C	0.897813	2.943375	0.000000
C	-0.232123	3.779141	0.000000
C	-1.306985	2.906087	0.000000
C	0.214370	-1.568725	2.583379
C	-1.044195	-1.605367	3.194731
C	-1.881225	-0.932444	2.315351
C	0.214370	-1.568725	-2.583379
C	-1.044195	-1.605367	-3.194731
C	-1.881225	-0.932444	-2.315351
B	-1.577463	0.295365	0.000000
H	1.159683	-1.971179	2.915839
H	-1.306769	-2.056956	4.137937
H	1.159683	-1.971179	-2.915839
H	-1.306769	-2.056956	-4.137937
H	-2.762362	0.467044	0.000000
H	1.946395	3.204288	0.000000
H	-0.260930	4.857417	0.000000
H	-2.936310	-0.714169	-2.372322
H	-2.936310	-0.714169	2.372322
H	-2.370138	3.092392	0.000000
F	3.232144	-0.379322	0.000000

[Zn(L)F]

Zn	1.452540	0.002071	0.000000
N	0.274022	1.714541	0.000000
N	-1.063244	1.459644	0.000000
N	0.276405	-0.857055	1.483946

```
N    -1.061343            -0.731527     1.264840
N     0.276405            -0.857055    -1.483946
N    -1.061343            -0.731527    -1.264840
C     0.423377             3.040972     0.000000
C    -0.829007             3.668958     0.000000
C    -1.742209             2.624920     0.000000
C     0.428153            -1.520395     2.632244
C    -0.823051            -1.836642     3.177429
C    -1.738156            -1.315655     2.274595
C     0.428153            -1.520395    -2.632244
C    -0.823051            -1.836642    -3.177429
C    -1.738156            -1.315655    -2.274595
B    -1.594721            -0.001322     0.000000
H     1.419145            -1.734755     3.004773
H    -1.031355            -2.366371     4.093257
H     1.419145            -1.734755    -3.004773
H    -1.031355            -2.366371    -4.093257
H    -2.791840            -0.001642     0.000000
H     1.413669             3.472322     0.000000
H    -1.039324             4.726559     0.000000
H    -2.817187            -1.320301    -2.281471
H    -2.817187            -1.320301     2.281471
H    -2.821267             2.631204     0.000000
F     3.276926             0.004770     0.000000
```

Calculated electronic energy (E, a.u.), HOMO/LUMO energies (eV), metal-ligand distances (Å), atomic charges, q(NPA) and spin densities, s(MPA) and s(NPA), at the B3LYP/6-311+G(d) levels.

[Mn(L)F]

```
E= -1953.568956  a.u. S**2= 8.755
Alpha HOMO= -6.637  LUMO= -0.653 Gap= 5.984 eV
Beta  HOMO= -7.050  LUMO= -1.161 Gap= 5.889 eV
--- GEOMETRY ---
1-28    1-2     1-4     1-6
1.868   2.184   2.184   2.184
--- WATCHED ATOMS ---
        Mn(1)  N(2)   N(4)   N(6)   F(28)
q(NPA): 1.548 -0.451 -0.451 -0.451 -0.800
s(MPA): 4.916 -0.017 -0.017 -0.017  0.091
s(NPA): 4.683  0.038  0.038  0.038  0.120
```

[Fe(L)F]

```
E= -2066.258798  a.u. S**2= 6.010
Alpha HOMO= -6.984  LUMO= -0.688 Gap= 6.296 eV
Beta  HOMO= -5.558  LUMO= -1.665 Gap= 3.893 eV
--- GEOMETRY ---
 1-28    1-2     1-4     1-6
 1.819   2.148   2.118   2.118
--- WATCHED ATOMS ---
        Fe(1)  N(2)   N(4)   N(6)   F(28)
q(NPA): 1.489 -0.428 -0.445 -0.445 -0.762
s(MPA): 3.823  0.034  0.015  0.015  0.129
s(NPA): 3.656  0.066  0.048  0.048  0.152
```

[Co(L)F]

```
E= -2185.300554  a.u. S**2= 3.757
Alpha HOMO= -7.064  LUMO= -0.674 Gap= 6.390 eV
```

```
Beta  HOMO= -6.619  LUMO= -2.145 Gap= 4.475 eV
--- GEOMETRY ---
 1-28    1-2     1-4     1-6
 1.816   2.066   2.067   2.067
--- WATCHED ATOMS ---
        Co(1)  N(2)   N(4)   N(6)   F(28)
q(NPA): 1.465 -0.432 -0.432 -0.432 -0.771
s(MPA): 2.778  0.044  0.044  0.044  0.124
s(NPA): 2.663  0.067  0.066  0.066  0.131
```

[Ni(L)F]

```
E= -2310.830622  a.u. S**2= 2.004
Alpha HOMO= -7.061  LUMO= -0.705 Gap= 6.357 eV
Beta  HOMO= -7.051  LUMO= -2.327 Gap= 4.724 eV
--- GEOMETRY ---
 1-28    1-2     1-4     1-6
 1.828   2.025   2.031   2.031
--- WATCHED ATOMS ---
        Ni(1)  N(2)   N(4)   N(6)   F(28)
q(NPA): 1.434 -0.415 -0.420 -0.420 -0.801
s(MPA): 1.700  0.096  0.082  0.082  0.089
s(NPA): 1.660  0.095  0.081  0.081  0.091
```

[Cu(L)F]

```
E= -2442.978536  a.u. S**2= 0.752
Alpha HOMO= -6.926  LUMO= -0.847 Gap= 6.080 eV
Beta  HOMO= -6.924  LUMO= -4.068 Gap= 2.855 eV
--- GEOMETRY ---
 1-28    1-2     1-4     1-6
 1.813   2.244   1.984   1.984
--- WATCHED ATOMS ---
        Cu(1)  N(2)   N(4)   N(6)   F(28)
q(NPA): 1.435 -0.426 -0.421 -0.421 -0.778
s(MPA): 0.679 -0.002  0.108  0.108  0.115
s(NPA): 0.696 -0.001  0.099  0.099  0.108
```

[Zn(L)F]

```
E= -2581.876960  a.u. S**2= 0.000
HOMO= -7.094  LUMO= -0.732 Gap= 6.361 eV
--- GEOMETRY ---
 1-28    1-2     1-4     1-6
 1.824   2.079   2.079   2.079
--- WATCHED ATOMS ---
        Zn(1)  N(2)   N(4)   N(6)   F(28)
q(NPA): 1.669 -0.476 -0.475 -0.475 -0.865
s(MPA): 0.000  0.000  0.000  0.000  0.000
s(NPA): 0.000  0.000  0.000  0.000  0.000
```

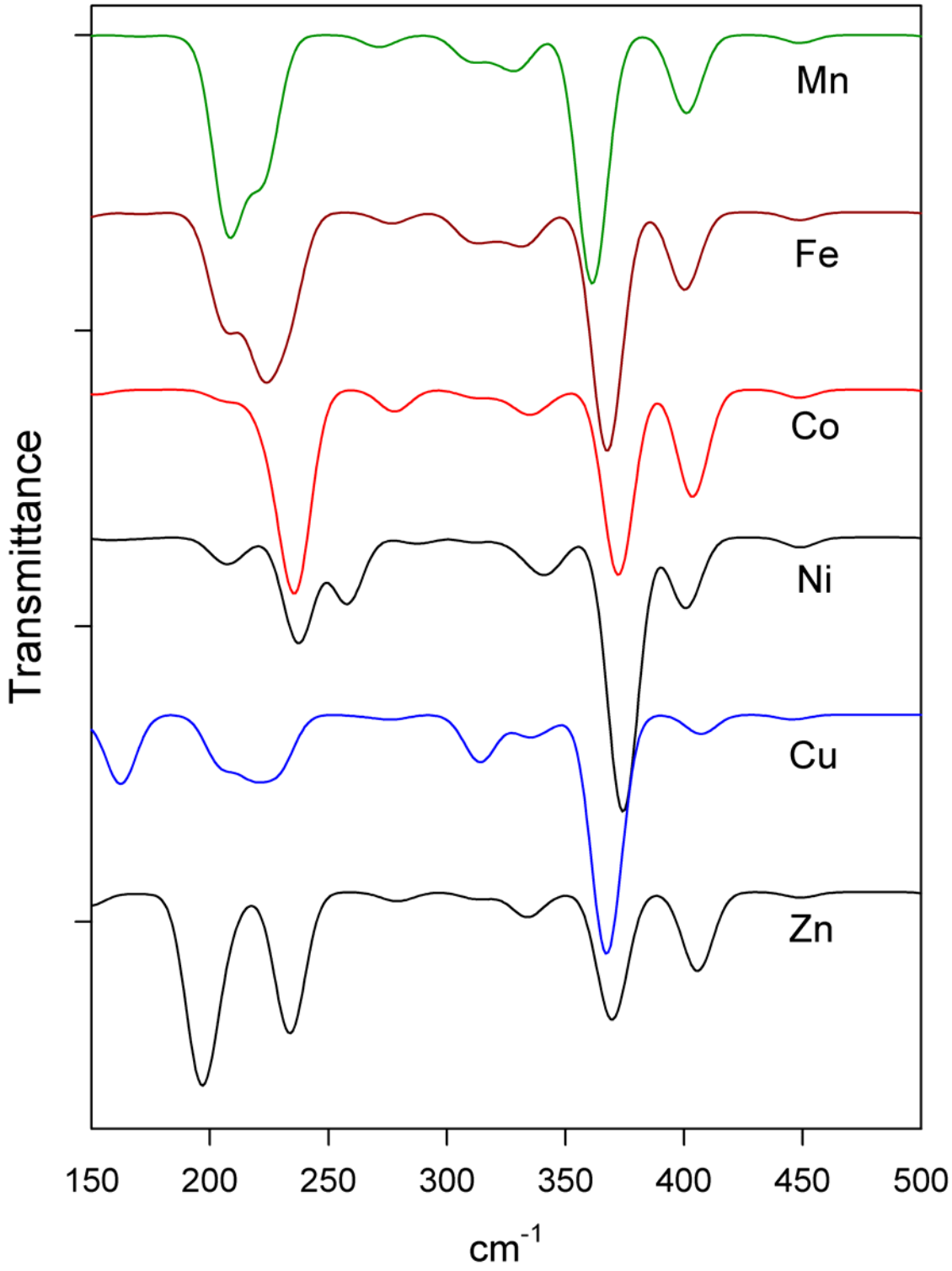


Figure S1. Calculated IR spectra of the [ML(SC_6F_5)] complexes.

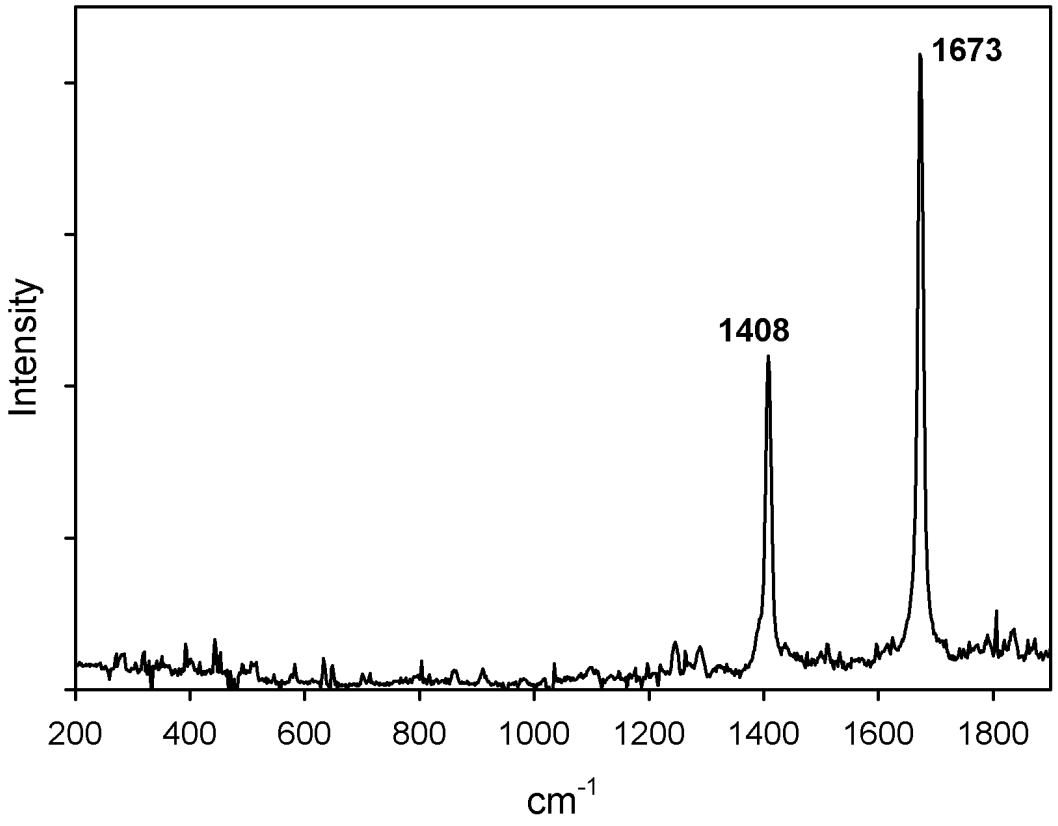


Figure S2. Resonance Raman spectrum of [NiL(SC_6F_5)], (excitation wavelength λ_o 351 nm).

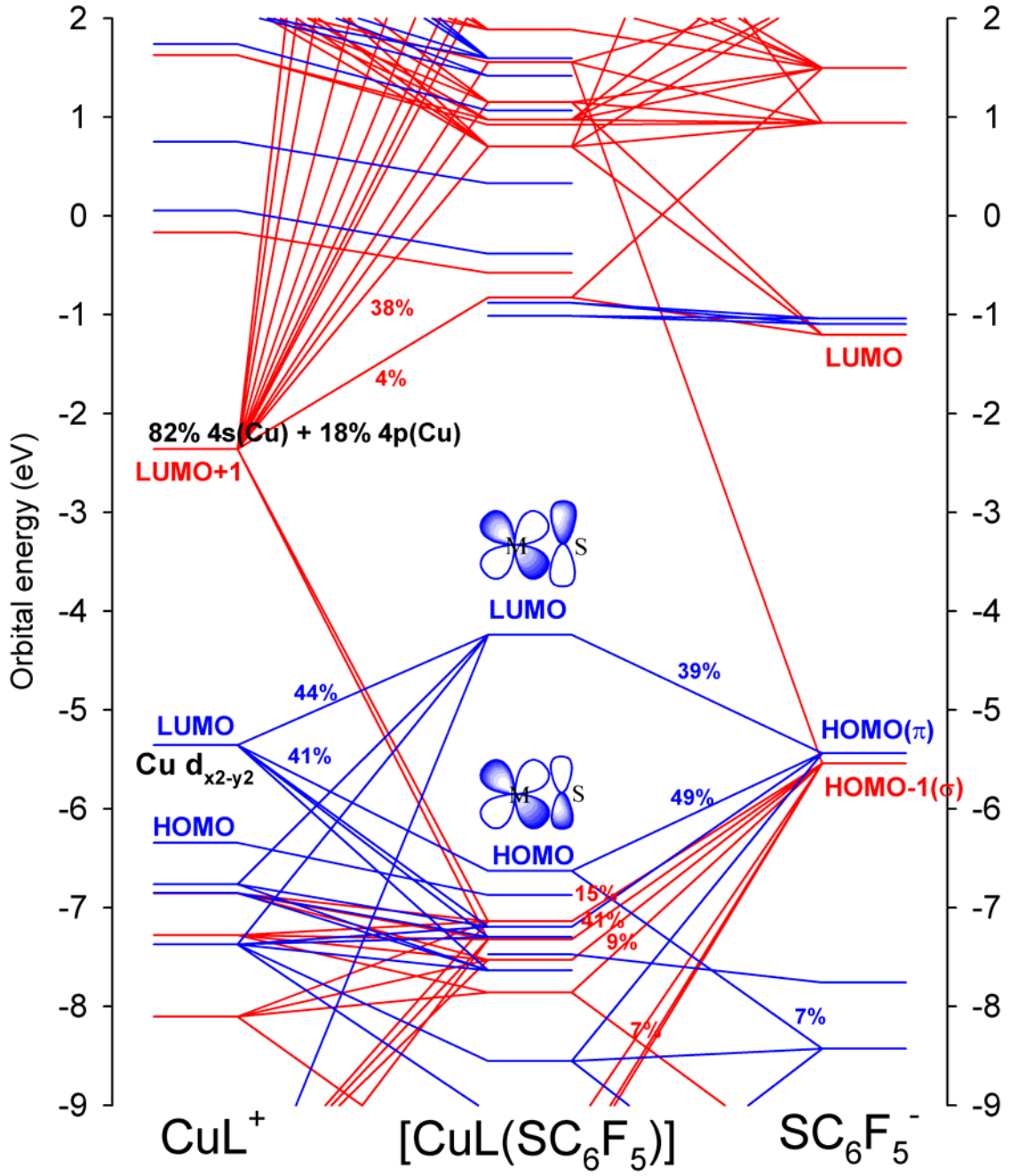


Figure S3. β-Spin orbital interaction diagram illustrating the coupling of the metal and thiolate fragments in the [CuL(SC_6F_5)] complex (the *AOMix-CDA* calculation, based on B3LYP/TZVP results; MOs with *a'* and *a"* symmetry are shown in red and blue respectively; molecular orbitals of the ML^+ and $SC_6F_5^-$ fragments are shifted by 4.0 and -4.5 eV respectively; lines connect all MO-FO orbital pairs with the corresponding MO-FO character greater than 1.9%).

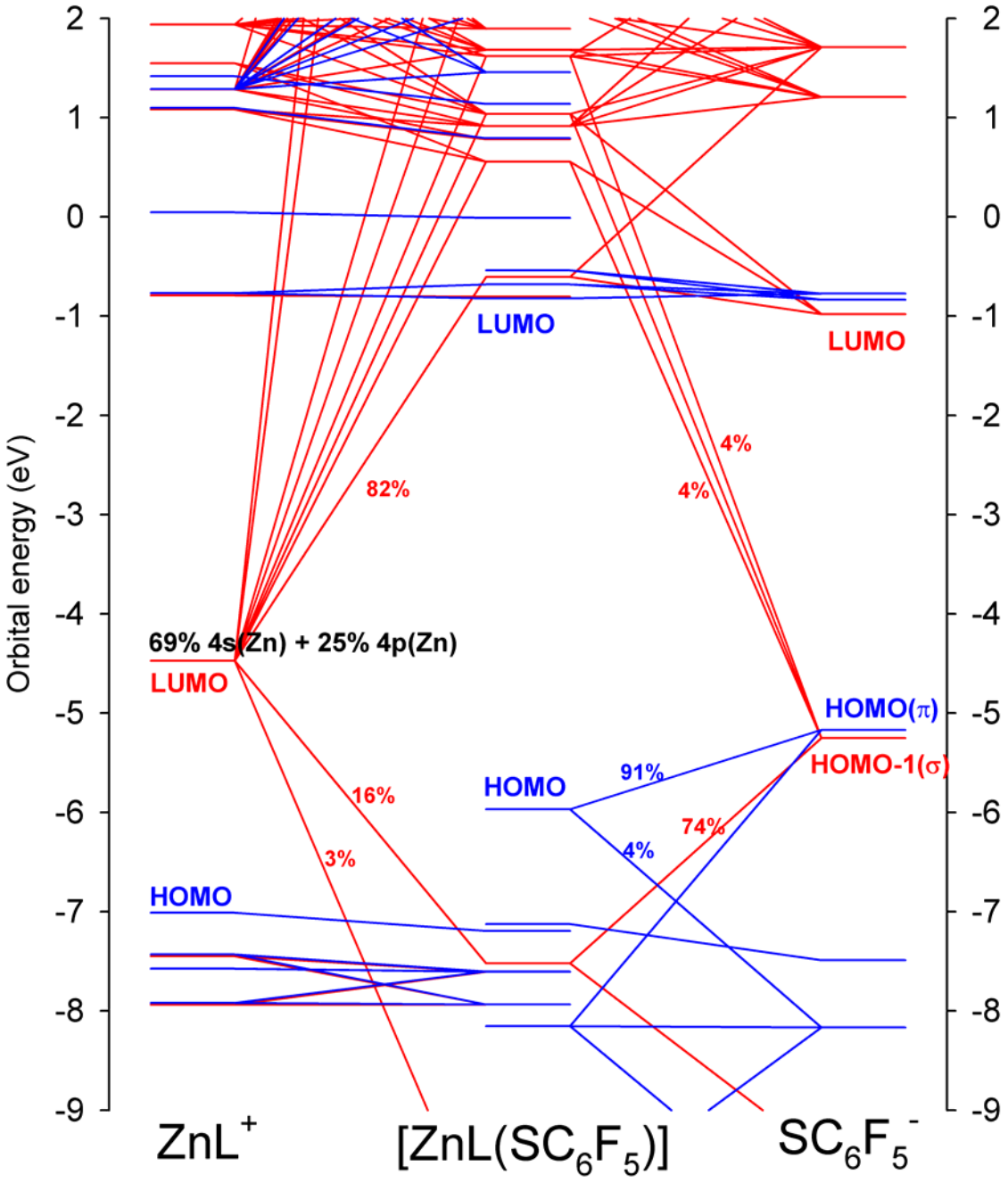


Figure S4. Orbital interaction diagram illustrating the coupling of the metal and thiolate fragments in the [ZnL(SC_6F_5)] complex (the *AOMix-CDA* calculation, based on B3LYP/TZVP results; MOs with *a'* and *a"* symmetry are shown in red and blue respectively; molecular orbitals of the ML^+ and $SC_6F_5^-$ fragments are shifted by 3.3 and -4.2 eV respectively; lines connect all MO-FO orbital pairs with the corresponding MO-FO character greater than 1.9%).

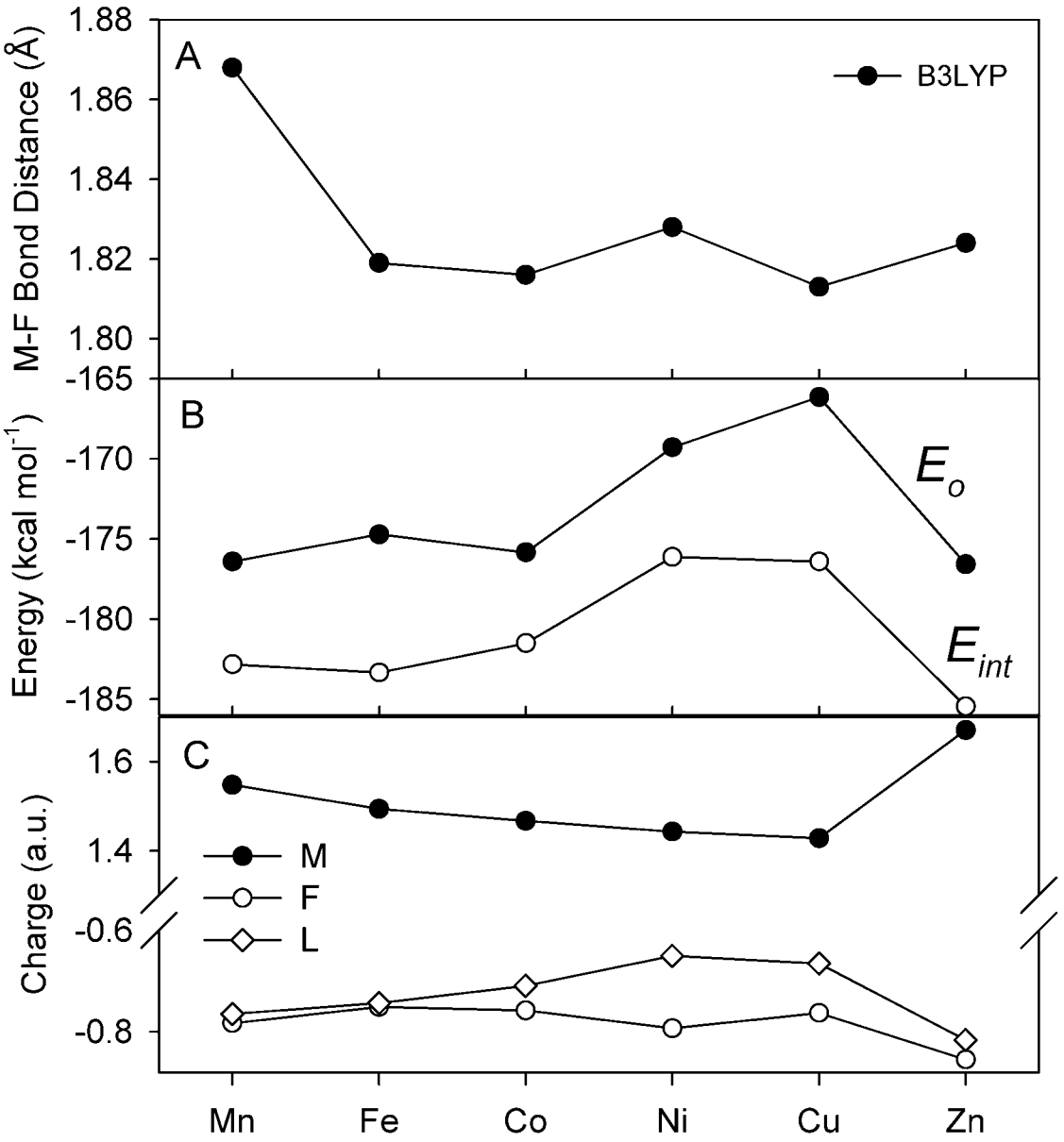


Figure S5. A) Calculated M-S bond lengths in the [ML(F)] complexes; B) calculated binding energies, E_o, and interaction energies, E_{int}, between the ML^+ and F^- fragments; and C) the NPA charges of the metal and fluorine atoms and the pyrazolyl ligand L.

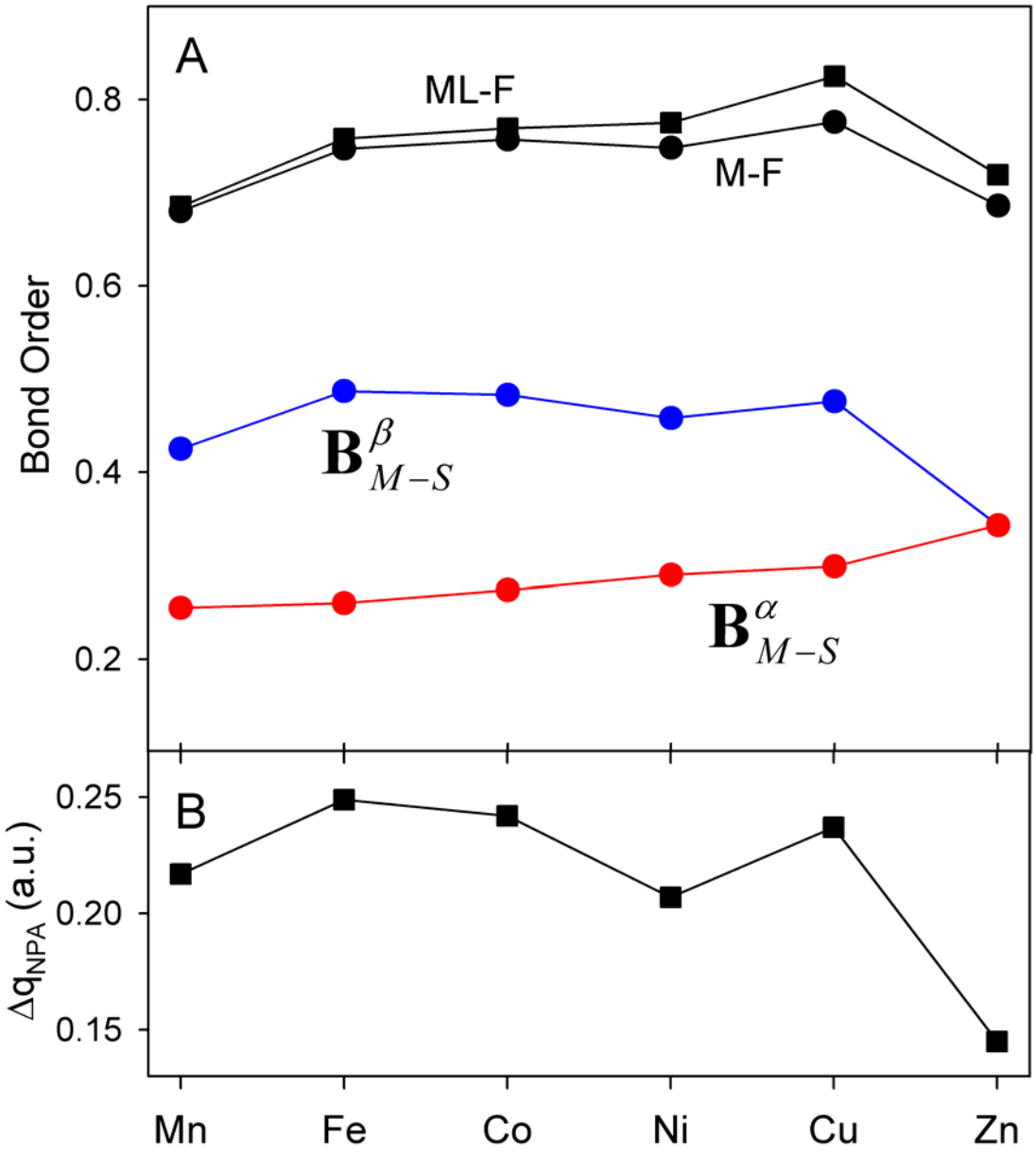


Figure S6. A) The M-S bond order (black circles) and its α-spin and β-spin orbital components (red and blue circles, respectively) and the bond order between the ML^+ and F^- fragments (black squares) in the [ML(F)] complexes and B) the charge donation from the F^- ligand to the ML^+ fragment.

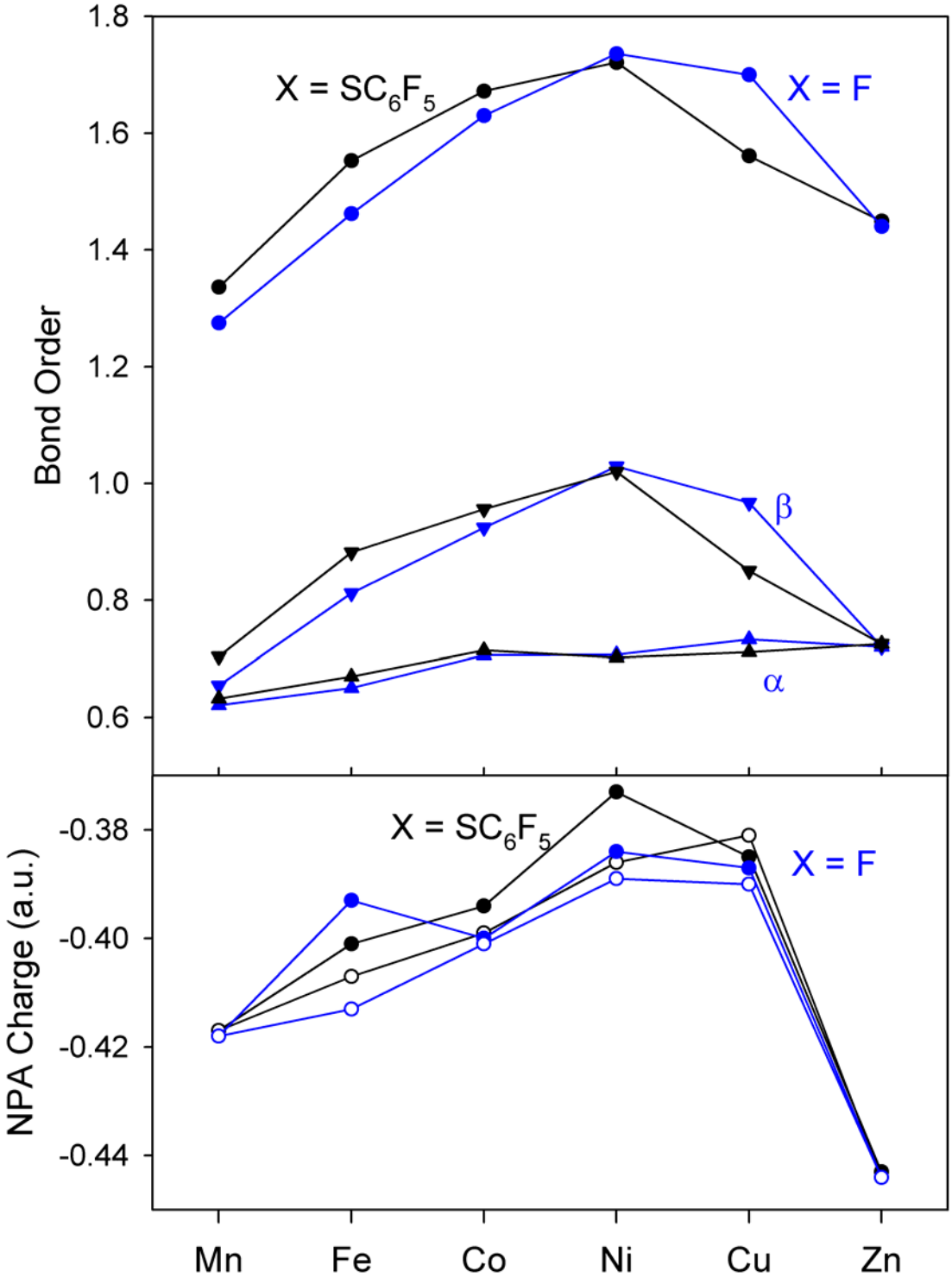


Figure S7. A) The metal - pyrazolyl ligand bond orders (solid circles) and its α- and β-MO components (upper triangles and lower triangles, respectively) and the bond order and B) The NPA charges of N2,N4, and N6 atoms of pyrazolyl ligand. The data for the [ML(SC_6F_5)] and [ML(F)] complexes are shown in black and blue respectively.