Supplementary Materials

ADF Computational Details:

DFT Calculations are performed as listed in the experimental section using primary input parameters as listed below. Complete output and input files are available directly from the authors; most output files exceed 500Mb per calculation.

Primary ADF Input File Parameters:

```
scf
  converge    0.00000001
  mixing      0.1
  iterations  200
end
xc
  lda scf    vwn
  gga scf    becke perdew
end
integration 5.00
unrestricted
```

DFT Computational Geometries:

```
[Fe(SCH3)4]2-                        [Fe(SCH3)4]1-
     Fe   0.000   0.000   0.000     Fe    .0000     .0000     .0000
     S   -1.347   1.347   1.242     S   -1.3443    1.3443    1.2292
     S   -1.347  -1.347  -1.222     S   -1.3443   -1.3443   -1.2292
     S    1.347  -1.347   1.242     S    1.3443   -1.3443    1.2292
     S    1.347   1.347  -1.222     S    1.3443    1.3443   -1.2292
     C   -2.207   0.235   2.289     C   -2.1955     .2348    2.2864
     C   -0.235  -2.207  -2.269     C    -.2348   -2.1955   -2.2864
     C    2.207  -0.235   2.289     C    2.1955    -.2348    2.2864
     C    0.235   2.207  -2.269     C     .2348    2.1955   -2.2864
     H   -2.903   0.807   2.942     H   -2.8200     .7505    2.8729
     H   -1.549  -0.261   2.854     H   -1.5332    -.2574    2.8512
     H   -2.727  -0.410   1.730     H   -2.7149    -.4163    1.7329
     H   -0.807  -2.903  -2.922     H    -.7505   -2.8200   -2.8729
     H    0.410  -2.727  -1.710     H     .4163   -2.7149   -1.7329
     H    0.261  -1.549  -2.834     H     .2574   -1.5332   -2.8512
     H    2.903  -0.807   2.942     H    2.8200    -.7505    2.8729
     H    1.549   0.261   2.854     H    1.5332     .2574    2.8512
     H    2.727   0.410   1.730     H    2.7149     .4163    1.7329
     H    0.807   2.903  -2.922     H     .7505    2.8200   -2.8729
     H   -0.410   2.727  -1.710     H    -.4163    2.7149   -1.7329
     H   -0.261   1.549  -2.834     H    -.2574    1.5332   -2.8512

[FeCl4]2-                            [FeCl4]1-
     Fe   0.000   0.000   0.000     Fe    .0000     .0000     .0000
     Cl  -1.352   1.352   1.235     Cl  -1.3020    1.3020    1.1850
     Cl  -1.352  -1.352  -1.235     Cl  -1.3020   -1.3020   -1.1850
     Cl   1.352  -1.352   1.235     Cl   1.3020   -1.3020    1.1850
     Cl   1.352   1.352  -1.235     Cl   1.3020    1.3020   -1.1850
```

VBCI Simulations (TT-MULT):

Representative RCG Input File:

```
   10    0    0   14    0    0    1    1  INTER0
    0                        70997070            8065.47800     0000000
    1     3 1 13 1 10         00      5 00000000   8065.4780 .00     0 1
P06  D06  P00
P06  D05  P01
Fe2+    1 1
Fe2+    2 1
                    -99999999.
   10    0    0   14    0    0    1    1  INTER0
    0                        64998080            8065.47800     0000000
    1     4 1 14 1 10         00      5 00000000   8065.4780 .00     0 1
```

```
P06  D07  D09  P00
P06  D06  D09  P01
Fe2+    1 2
Fe2+    2 2
                    -99999999.
   10    0    0   14    0    4    0    4  INTER2 shell03000000 spin03000000
    0                         64998080            8065.47800     0000000
    1     3 1 13 1 10          00      5 00000000   8065.4780 .00     0 1
P06  D06  D10
P06  D07  D09
Fe2+ 2P06 3D06     4     .0000   10.9661    6.8151     .0522     .0000HR99999999
Fe2+ 2P06 3D07     4     .0000    9.7621    6.0181     .0462     .0000HR99999999
                    -99999999.
   10    0    0   14    0    4    0    4  INTER2 shell03000000 spin03000000
    0                         64998080            8065.47800     0000000
    1     4 1 14 1 10          00      5 00000000   8065.4780 .00     0 1
P06  D05  D10  P01
P06  D06  D09  P01
Fe2+ 2P06 3D05 P   4     .0000   12.0431    7.5351     .0592     .0000HR99999999
Fe2+ 2P06 3D06 P   4     .0000   10.9661    6.8151     .0522     .0000HR99999999
                    -99999999.
   -1
```

Representative RAC Input File:

```
Y
    % vertical 1 1
 racer O3
   to  OH
 endchain
 actor   1- multipole   transi
   oper     MULTIPOLE
     branch  1- > 0 1-  1.000
 actor   0+ HAMILTONIAN ground
 actor   0+ 10Dq        ground
 actor   0+ HAMILTONIAN excite
 actor   0+ 10Dq        excite
RUN
      % vertical 2 2
 racer O3
   to  OH
 endchain
 actor   1- multipole   transi
   oper     MULTIPOLE
     branch  1- > 0 1-  1.000
 actor   0+ HAMILTONIAN ground
 actor   0+ 10Dq        ground
 actor   0+ HAMILTONIAN excite
 actor   0+ 10Dq        excite
RUN
     % horizontal ground   1 2
 racer O3
 to    OH
 endchain
 actor   0+ Eghybr      transi
   oper     MULTIPOLE
     branch  0+ > 0 0+   .894427191
     branch  4+ > 0 0+  3.286335345
 actor   0+ T2ghybr     transi
   oper     MULTIPOLE
     branch  0+ > 0 0+  1.341640787
     branch  4+ > 0 0+ -3.286335345
 actor   0+ HAMILTONIAN ground
   oper     HAMILTONIAN
     branch  0+ > 0 0+  1.000
 actor   0+ 10Dq        ground
   oper     SHELL2
     branch  4+ > 0 0+  3.286335345
 actor   0+ HAMILTONIAN excite
   oper     HAMILTONIAN
     branch  0+ > 0 0+  1.000
```

```
 actor   0+ 10Dq        excite
   oper     SHELL2
     branch  4+ > 0 0+  3.286335345
RUN
    %  horizontal excite 1 2
 racer O3
 to    OH
 endchain
 actor   0+ Eghybr      transi
   oper     MULTIPOLE
     branch  0+ > 0 0+   .894427191
     branch  4+ > 0 0+  3.286335345
 actor   0+ T2ghybr     transi
   oper     MULTIPOLE
     branch  0+ > 0 0+  1.341640787
     branch  4+ > 0 0+ -3.286335345
 actor   0+ HAMILTONIAN ground
   oper     HAMILTONIAN
     branch  0+ > 0 0+  1.000
 actor   0+ 10Dq        ground
   oper     SHELL2
     branch  4+ > 0 0+  3.286335345
 actor   0+ HAMILTONIAN excite
   oper     HAMILTONIAN
     branch  0+ > 0 0+  1.000
 actor   0+ 10Dq        excite
   oper     SHELL2
     branch  4+ > 0 0+  3.286335345
RUN
```

Representative BAN Input File (XPS):

```
PRMULT
NCONF 2 2
erange 0.5
N2 1
def EG2 = 0.3 unity
def EF2 = 0.3 unity
XMIX 2  0.5 1.0
 2   1 1 2          2 1 2
XHAM 2  1.0 -0.2
 4   1 1   1 2   2 1   2 2
TRAN  2    1 1    2 2
TRIADS
          0+    1-    1-  0
          1+    1-    0-  0
          1+    1-    1-  0
          1+    1-    2-  0
          1+    1-   ^1-  0
          2+    1-    1-  0
          2+    1-   ^1-  0
         ^1+    1-    1-  0
         ^1+    1-    2-  0
         ^1+    1-   ^1-  0
         ^1+    1-   ^0-  0
         ^0+    1-   ^1-  0
```