CHEMISTRY
A EUROPEAN JOURNAL

# Supporting Information

# The Electronic Structure of Iron Corroles: A Combined Experimental and Quantum Chemical Study

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Table S1. Compatibility table of the involved MOs.

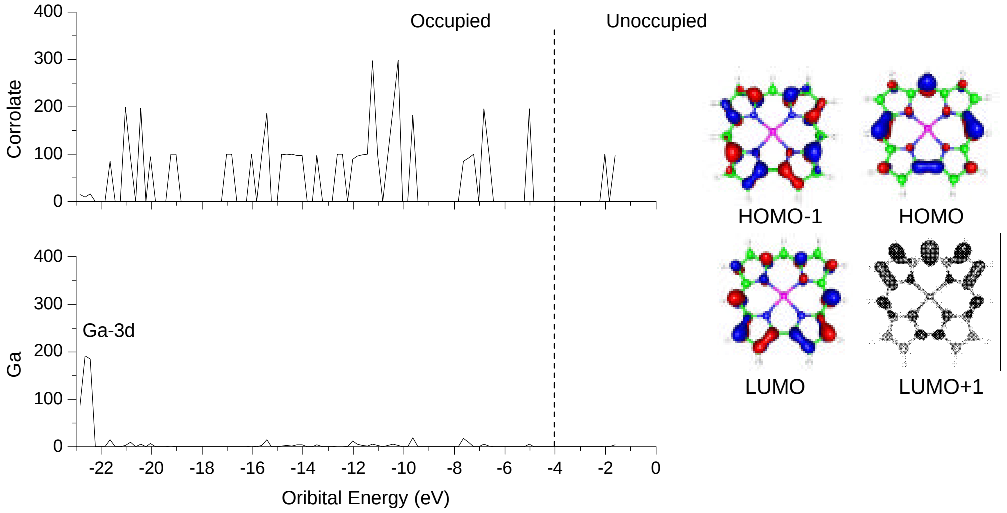
| | Porphyrin | | Corrole | |
|---|---|---|---|---|
| | $D_{4h}$ | $C_{4v}$ | $C_{2v}$ | $C_s$ |
| HOMO | $a_{2u}$ | $a_1$ | $b_1$ | a' |
| HOMO-1 | $a_{1u}$ | $a_2$ | $a_2$ | a'' |
| Fe-$d_{z2}$ | $a_{1g}$ | $a_1$ | $a_1$ | a' |

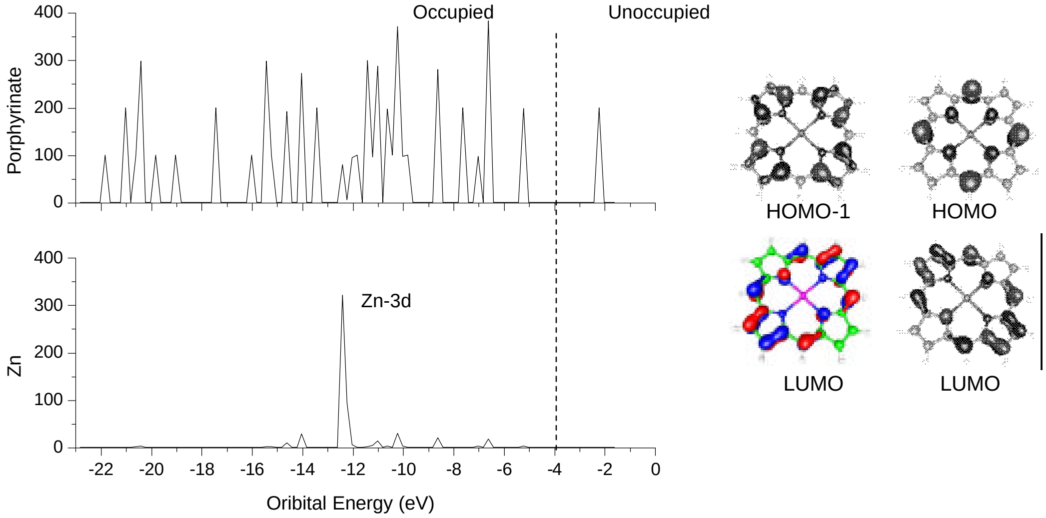
Table S2. Calculated exchange coupling constants and corresponding orbital overlaps employed the B3LYP density functional at the BP86 geometries for the range of complexes studied in this work.

| | $J$ ($cm^{-1}$) | UCO overlap |
|---|---|---|
| $[Fe(TPP)Cl]^+$ | -217 | 0.41 |
| $[Fe(TTP)Cl]^+$ | -8 | 1 |
| Fe(TPFC)F | -565 | 0.52 |
| Fe(TPFC)Cl | -602 | 0.58 |
| Fe(TPFC)Br | -652 | 0.59 |
| Fe(TPFC)I | -729 | 0.66 |
| Fe(TDCC)Cl | -619 | 0.57 |
| Fe(TDCC)Br | -655 | 0.59 |
| Fe(TDCC)I | -740 | 0.66 |

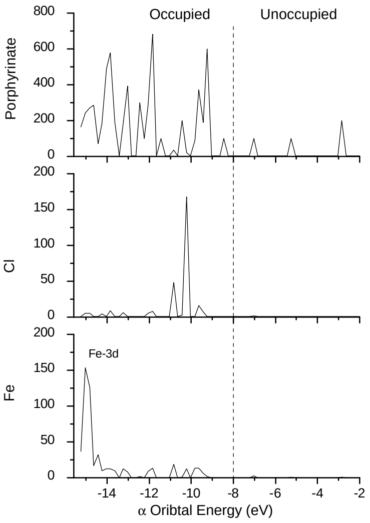
### Orbital Energies.

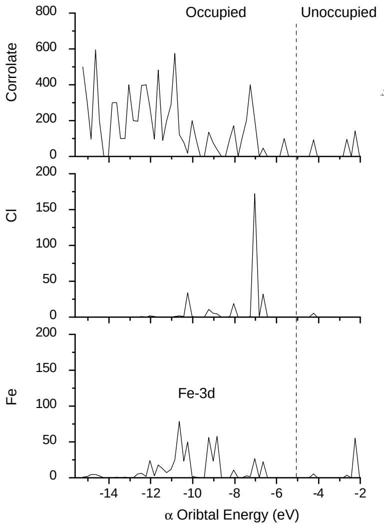
Initially two neutral model complexes for these two systems, Zn(II)porphoryrinate and Ga(III)corrolate, were chosen to investigate the relative energy of the high lying occupied p orbitals in corrole and porphyrin systems. It turned out that the relevant p-orbital of the corrole is situated at a slightly higher energy (~0.3 eV) than the analogous porphyrin orbital. This can be seen in the plots below that show the percentage fragment character as a function of orbital energy (a kind of density of “states” plot, similar to what the physicist’s often do).





For the two iron complexes we cannot seriously compare the absolute orbital energies since they differ by one unit in their total charge. There is another key factor to understanding the electronic structure differences in these systems: in the porphyrin, the iron is high-spin (S = 5/2) while in the corrole the iron is intermediate spin (S = 3/2). As already mentioned in the main body of the paper, the reason for this is the much stronger s -interaction in the corrole that makes the $d_{x2-y2}$ orbital energetically unavailable. As a result of the high-spin configuration, the occupied spin-up orbitals in the iron-porphyrin are much more stabilized by spin polarization than the corresponding corrole orbitals: the energy difference of the metal d and the macrocyclic p orbitals is ~3 eV in the corrole complex and ~7 eV in the porphyrin complex. Hence, the interaction of the iron d-orbitals with the ring orbitals is much stronger in the spin-up as well as the spin-down manifold in the corrole system. Note that the unoccupied a-LUMO is the spin-up counterpart of the occupied ß-HOMO. This corroborates our suggested electronic structures for the two complexes in the manuscript.


Occupied
Unoccupied
Porphyrinate
800
600
400
200
0
Cl
200
150
100
50
0
Fe
200
150
100
50
0
Fe-3d
-14
-12
-10
-8
-6
-4
-2
α Oribtal Energy (eV)


Occupied
Unoccupied
Corrolate
800
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Cl
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0
Fe
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Fe-3d
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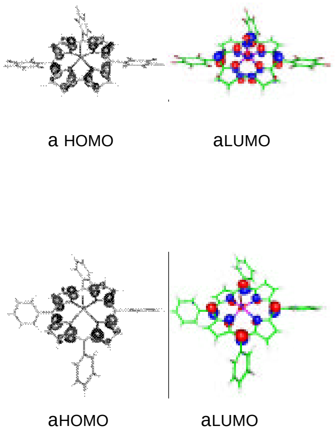
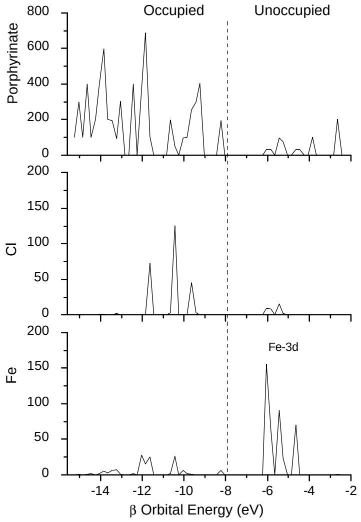
-10
-8
-6
-4
-2
α Oribtal Energy (eV)


a HOMO
aLUMO
aHOMO
aLUMO


Occupied
Unoccupied
Porphyrinate
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Fe
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100
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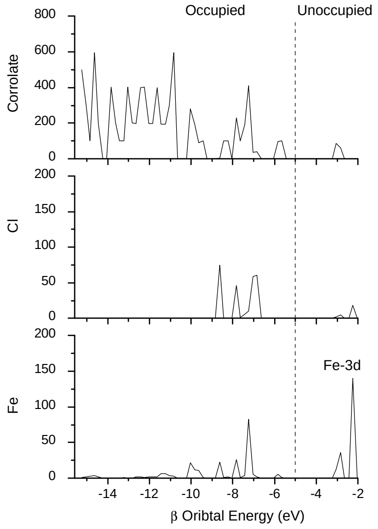
Fe-3d
-14
-12
-10
-8
-6
-4
-2
β Orbital Energy (eV)


Occupied
Unoccupied
Corrolate
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Cl
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Fe
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Fe-3d
-14
-12
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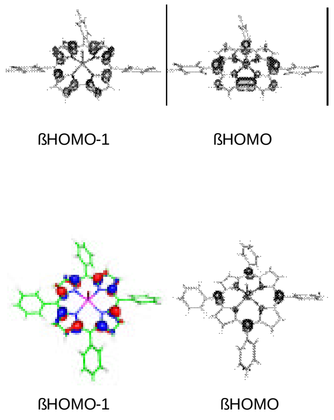
-4
-2
β Orbital Energy (eV)


ßHOMO-1
ßHOMO
ßHOMO-1
ßHOMO