Supplementary data

Directly linked metalloporphyrins: A quest for the bio-inspired materials

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S1: Computational details associated with the calculations based on probe particle model.

S2: DFT computed spin-density maps for the four system.

S3: Additional details about the DFT-NEGF calculations.

S4: Theoretical details of the Localize Orbital Locator (LOL) scheme and corresponding LOL maps.

S5: Projected density of states (PDOS) plots of the model system.

S6: Optimized coordinates of the four diporphyrin systems considered in the present study.

S1. Computational details associated with the calculations based on probe particle model.

All computations involving surfaces were carried out using the Vienna *ab initio* simulation package while calculations on gas-phase molecules were performed also using VASP and/or GAUSSIAN09. VASP utilizes an iterative scheme to solve self-consistently the Kohn–Sham equations of density-functional theory using residuum-minimization techniques and an optimized charge-density mixing routine. A plane-wave basis set is employed to expand the electronic wave functions, which facilitates the evaluation of the Hellmann–Feynman forces acting on the atoms. Electron-ion interactions are modeled using ultrasoft pseudopotentials, which allows the use of a

low energy cutoff for the plane-wave basis set. For electron-electron exchange and correlation interactions the functional of Perdew and Wang (PW91) a form of the generalized gradient approximation, is used throughout. The relaxation of atom positions in the molecular structure is performed via the action of a conjugate gradient optimization procedure. In the GAUSSIAN calculations, cc-pVTZ basis sets is used for the molecular geometry optimization.

The silver surface was modeled by supercells consisting in most cases of four atomic layers separated by a vacuum region of ten-layer equivalent thickness; periodic boundary conditions are applied in all three Cartesian directions. The interlayer spacing is taken from the previously determined value of the bulk lattice parameter, 4.2 Å. A single molecule was placed in the vacuum region on the upper side of the slab. Geometry optimization of key binding configurations were performed using four atomic silver layers without dipole correction, while rough scans of large regions of the potential-energy surface were scanned through constrained geometry optimization using only two silver layers. In both cases, only the top Ag layer is optimized, the lower layers being frozen in order to mimic bulk silver. Spin polarization was not permitted in these calculations, a reasonable approximation as any unpaired spin is found to be associated with the bulk crystal rather than the molecule or interface.

Most calculations employed (3x3x1) superstructure resulting in nine Ag atoms per layer. The Brillouin-zone integrations have been conducted on a 3x3x1 k-point Monkhorst–Pack grid with a Methfessel– Paxton smearing of 0.2 eV, while denser meshes of 4x4x1, 5x5x1, and 6x6x1 have been used for the higher coverages. VASP calculations pertinent to gas-phase molecules employed cells of the same size as the supercells, an integration using the Γ-point only, and a Gaussian smearing of only 0.01 eV. An energy of 290 eV, dictated by the pseudopotential of carbon, has been set as the plane-wave basis-set cutoff in all computations.

S2. DFT computed spin-density maps for the four system.

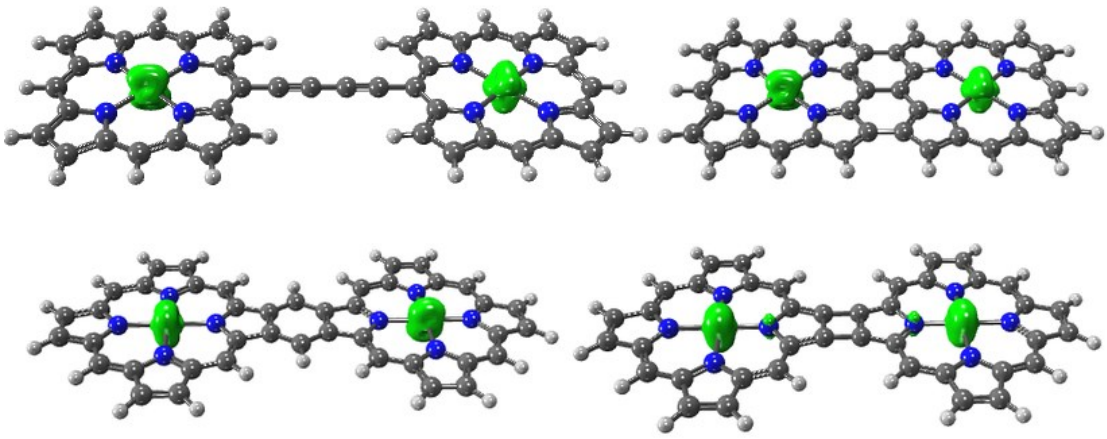

Figure S2: Spin-density maps for the model systems. The green isosurface represents the location of excess spin on the system.

S3. Additional details about the DFT-NEGF calculations.

Gas-phase calculations were executed using dispersion corrected PBE i.e., PBE(D3) exchange-correlation functional as enforced in ADF 2019.105 software. For the isolated diporphyrin system geometry optimization was performed at B3LYP/TZP level. The same level of theory has been maintained for the DFT-NEGF calculations, except considering a single-ζ basis set for gold atoms to maintain accuracy in the computations. Eventually, the density functional theory (DFT) approach coupled with the non-equilibrium Green's function (NEGF) technique was employed to illustrate the charge transport through the electrode-single molecule-electrode junction. Each electrode is designed with Au (111) faces consisting of 3 × 3 gold atoms. The transport calculations are done on the optimized geometries of the isolated molecules (HS or LS configurations), sandwiched by the atomic gold electrodes. The scalar relativistic ZORA (Zero Order Regular Approximation) is further granted for the DFT calculations. Theoretical conductance value G was determined from Landauer formula $G = G0 \times \tau(\varepsilon F)$ considering zero-bias approximation where $\tau(\varepsilon F)$ is the transmission function at the Fermi energy and (εF) Fermi energy of the electrode. In the context of the Landauer Formula, where the conductance is expressed as a sum over scattering channels of transmission coefficients, the transmission coefficients describe the probability that an electron from, let's say, the left lead is transmitted to

the right lead. The value of the transmission coefficients for each channel serves as a probability.

S4: Theoretical details of the Localize Orbital Locator (LOL) scheme.

Schmider and Becke in the paper J. Mol. Struct. (THEOCHEM), 527, 51 first proposed another function for locating high localization regions likewise ELF, defined by

$$\mathrm{LOL}(\mathbf{r}) = \frac{\tau(\mathbf{r})}{1+\tau(\mathbf{r})}$$

where

$$\tau(\mathbf{r}) = \frac{D_0(\mathbf{r})}{(1/2)\sum_i \eta_i \left|\nabla \varphi_i(\mathbf{r})\right|^2}$$

$D_0(r)$ for spin-polarized system and close-shell system are defined in the same way as in ELF.

LOL has similar expression compared to ELF (Electron Localization Function). Actually, the chemically significant regions that highlighted by LOL and ELF are generally qualitative comparable, while Jacobsen pointed out that LOL conveys more decisive and clearer picture than ELF, see Can. J. Chem., 86, 695. Obviously LOL can be interpreted in kinetic energy way as for ELF, however LOL can also be interpreted in view of localized orbital. Small (large) LOL value usually appears in boundary (inner) region of localized orbitals because the gradient of orbital wavefunction is large (small) in this area. The value range of LOL is identical to ELF, namely [0,1].

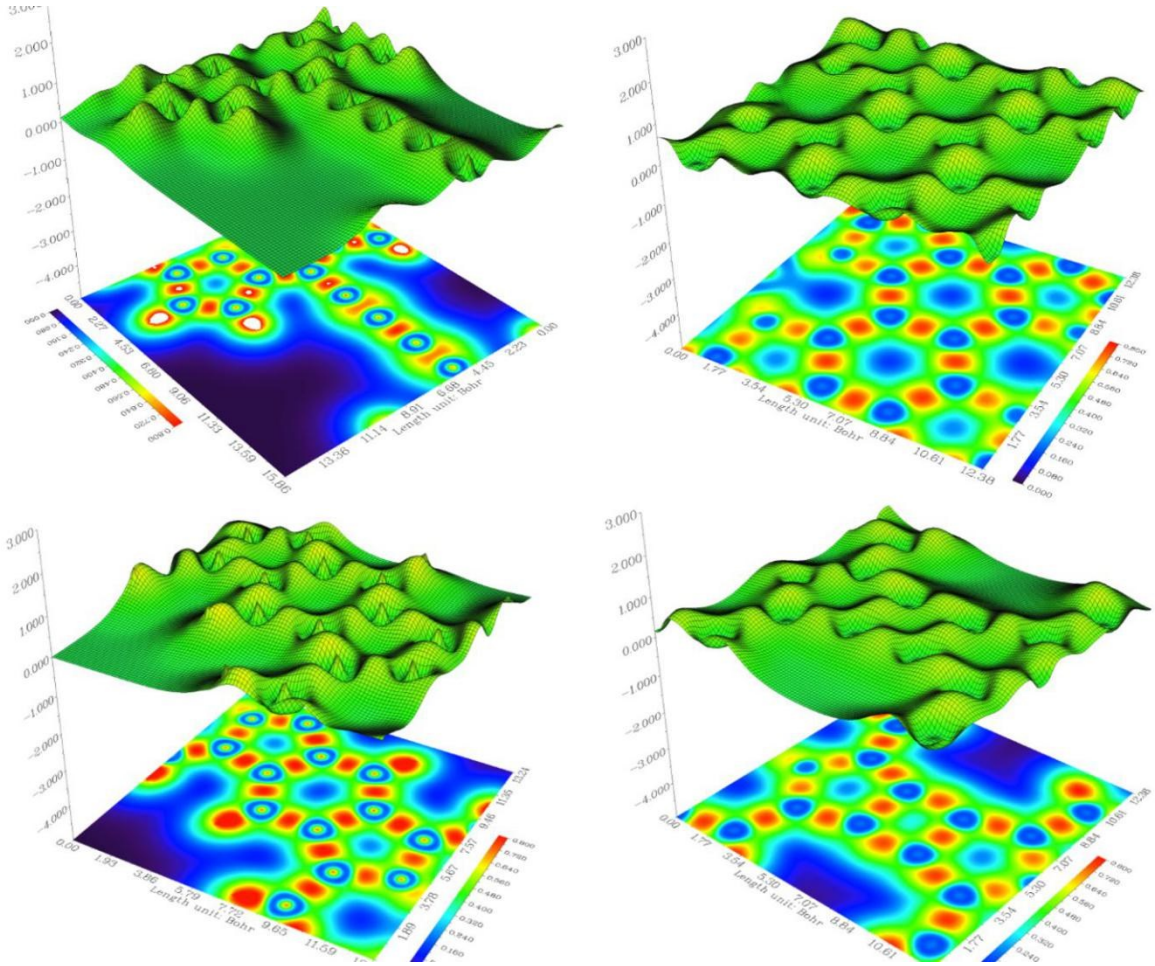

Figure S4: Localized Orbital Locator (LOL) map of the four systems.

S5: Projected density of states (PDOS) plots of the model system.

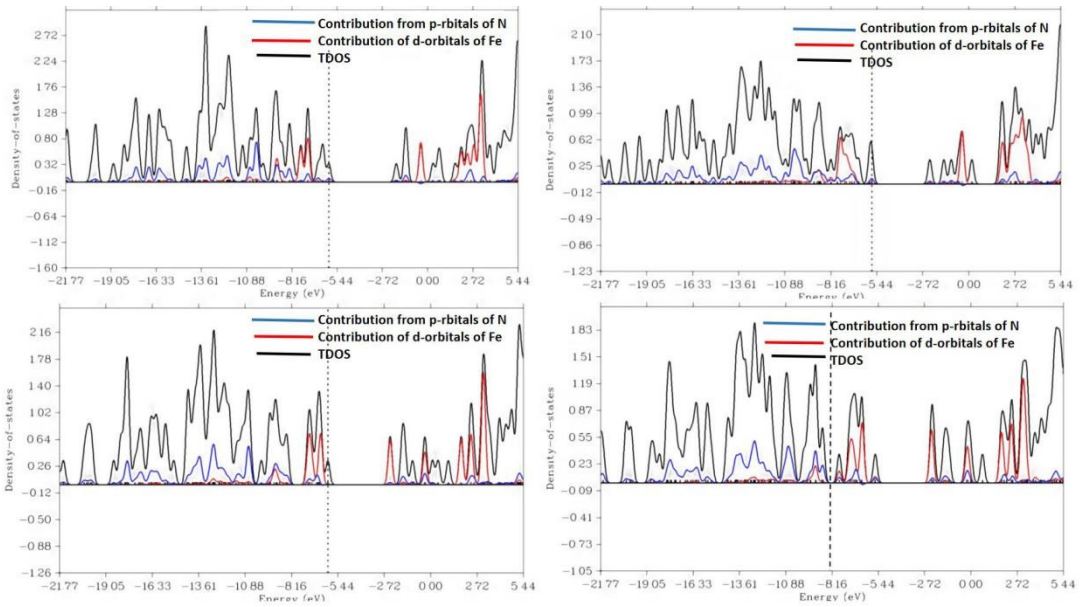

Figure S5: PDOS plots computed at CAM-B3LYP/ccpvTZ level of the four diporphyrin systems considered in the present study.

S6: Optimized coordinates at CAM-B3LYP/ccpvTZ level of the four diporphyrin systems considered in the present study.

(i) System 1

76

symmetry c1

N	-5.323756000	-1.409382000	-0.000084000
N	8.169753000	-1.413175000	-0.000075000
N	-8.169750000	-1.413173000	0.000106000
N	5.323759000	-1.409390000	0.000006000
N	-8.169697000	1.413235000	0.000110000
N	5.323700000	1.409330000	0.000014000
N	-5.323704000	1.409339000	-0.000090000
N	8.169694000	1.413234000	-0.000079000
C	-5.524061000	-2.772791000	-0.000216000
C	7.981902000	-2.772157000	-0.000074000
C	-4.263244000	-3.459542000	-0.000254000
C	9.247762000	-3.452953000	-0.000106000
H	-4.148800000	-4.531118000	-0.000358000
H	9.367801000	-4.523954000	-0.000111000
C	-3.296861000	-2.510372000	-0.000117000

C	10.207623000	-2.495560000	-0.000130000
H	-2.228636000	-2.639687000	-0.000089000
H	11.278301000	-2.618591000	-0.000158000
C	-3.965479000	-1.237614000	-0.000031000
C	9.530878000	-1.227107000	-0.000109000
C	-3.301760000	-0.000059000	0.000026000
C	10.167866000	0.000072000	-0.000130000
C	-3.965434000	1.237520000	-0.000044000
C	9.530826000	1.227224000	-0.000120000
C	-3.296768000	2.510254000	-0.000147000
C	10.207518000	2.495705000	-0.000152000
C	-4.263116000	3.459460000	-0.000279000
C	9.247617000	3.453058000	-0.000130000
C	-5.523958000	2.772756000	-0.000230000
C	7.981785000	2.772209000	-0.000083000
C	-6.751336000	3.404886000	-0.000237000
C	6.751328000	3.404881000	-0.000039000
C	-7.981792000	2.772211000	-0.000044000
C	5.523951000	2.772748000	0.000012000
C	-9.247625000	3.453056000	0.000095000
C	4.263108000	3.459449000	0.000067000
H	-9.367621000	4.524062000	0.000011000
H	4.148621000	4.531020000	0.000077000

C	-10.207524000	2.495702000	0.000356000
C	3.296762000	2.510240000	0.000101000
H	-11.278197000	2.618775000	0.000527000
H	2.228532000	2.639512000	0.000145000
C	-9.530829000	1.227222000	0.000349000
C	3.965430000	1.237508000	0.000067000
C	-10.167866000	0.000068000	0.000485000
C	3.301760000	-0.000073000	0.000077000
C	-9.530875000	-1.227109000	0.000336000
C	3.965482000	-1.237626000	0.000045000
C	-10.207617000	-2.495564000	0.000324000
C	3.296868000	-2.510386000	0.000057000
H	-11.278294000	-2.618598000	0.000483000
H	2.228643000	-2.639704000	0.000089000
C	-9.247753000	-3.452954000	0.000067000
C	4.263253000	-3.459554000	0.000012000
H	-9.367789000	-4.523955000	-0.000025000
H	4.148812000	-4.531130000	0.000002000
C	-7.981894000	-2.772155000	-0.000057000
C	5.524068000	-2.772800000	-0.000011000
C	-6.751462000	-3.404876000	-0.000237000
C	6.751471000	-3.404881000	-0.000047000
H	-6.749786000	4.486080000	-0.000356000

H	6.749774000	4.486075000	-0.000042000
H	-6.749952000	-4.486070000	-0.000355000
H	6.749963000	-4.486075000	-0.000054000
H	-2.228538000	2.639529000	-0.000129000
H	11.278191000	2.618782000	-0.000187000
H	-4.148632000	4.531032000	-0.000390000
H	9.367610000	4.524064000	-0.000143000
C	1.890348000	-0.000102000	0.000112000
C	0.675395000	-0.000117000	0.000130000
C	-1.890348000	-0.000085000	0.000104000
C	-0.675395000	-0.000102000	0.000132000
Fe	-6.746797000	0.000005000	0.000015000
Fe	6.746797000	0.000000000	-0.000034000
H	11.248983000	0.000095000	-0.000159000
H	-11.248983000	0.000088000	0.000672000

(ii) System 2

68

symmetry c1

N	13.133174000	4.097767000	3.145323000
N	21.494954000	4.199201000	3.036778000
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N	18.666160000	4.170554000	3.072261000

N	10.267005000	6.883508000	3.161335000
N	18.628780000	6.984939000	3.052369000
N	13.095796000	6.912152000	3.125470000
N	21.457318000	7.031059000	3.016683000
C	12.970954000	2.728079000	3.157340000
C	21.323045000	2.836813000	3.048547000
C	14.245226000	2.070894000	3.145545000
C	22.598521000	2.174360000	3.037679000
H	14.385206000	1.002358000	3.151437000
H	22.733612000	1.105133000	3.043644000
C	15.196378000	3.051704000	3.125979000
C	23.546075000	3.144529000	3.019299000
H	24.618133000	3.034801000	3.007108000
C	14.482944000	4.304164000	3.126266000
C	22.853525000	4.404002000	3.018750000
C	15.145112000	5.531691000	3.108672000
C	23.472338000	5.641389000	3.002180000
C	14.450606000	6.741306000	3.108999000
C	22.820869000	6.862017000	3.001138000
C	15.130587000	8.012127000	3.090766000
C	23.479832000	8.139289000	2.983423000
C	14.153776000	8.967545000	3.096620000
C	22.506903000	9.084179000	2.988183000

C	12.897388000	8.277054000	3.118010000
C	21.249440000	8.388413000	3.008944000
C	11.661259000	8.896169000	3.129231000
C	20.010233000	9.006176000	3.019778000
C	10.438911000	8.245895000	3.149316000
C	18.790999000	8.354627000	3.040191000
C	9.163438000	8.908349000	3.160375000
C	17.516725000	9.011812000	3.051931000
H	9.028343000	9.977575000	3.154276000
H	17.376746000	10.080347000	3.045914000
C	8.215888000	7.938183000	3.179108000
C	16.565576000	8.031004000	3.071646000
H	7.143833000	8.047914000	3.191520000
C	8.908438000	6.678710000	3.179703000
C	17.279012000	6.778543000	3.071482000
C	8.289628000	5.441324000	3.196493000
C	16.616845000	5.551017000	3.089120000
C	8.941096000	4.220695000	3.197303000
C	17.311351000	4.341401000	3.088753000
C	8.282131000	2.943422000	3.214938000
C	16.631366000	3.070580000	3.106869000
H	7.213365000	2.805489000	3.229239000
C	9.255055000	1.998530000	3.209816000

C	17.608176000	2.115161000	3.100919000
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H	17.496520000	1.043322000	3.110062000
C	10.512516000	2.694294000	3.188842000
C	18.864564000	2.805650000	3.079593000
C	11.751719000	2.076529000	3.177731000
C	20.100695000	2.186536000	3.068378000
H	11.647338000	9.977280000	3.121576000
H	19.995269000	10.087273000	3.011911000
H	11.766681000	0.995430000	3.185419000
H	20.114614000	1.105424000	3.075888000
H	24.548600000	8.277225000	2.969352000
H	14.265428000	10.039383000	3.087383000
H	22.613595000	10.156593000	2.978837000
Fe	11.698398000	5.486245000	3.153493000
Fe	20.063558000	5.596462000	3.044407000
H	24.553392000	5.655722000	2.988987000
H	7.208578000	5.426992000	3.209972000

(iii) System 3

74

symmetry c1

N	9.418180000	3.139219000	3.273861000

N	22.210356000	5.385390000	3.026854000
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N	20.250355000	3.345357000	3.118889000
N	9.340650000	7.143822000	3.143031000
N	18.184486000	5.309407000	3.081528000
N	11.406518000	5.179769000	3.180305000
N	20.172823000	7.349957000	2.987952000
C	8.335156000	2.288614000	3.317110000
C	23.062666000	4.307551000	3.052082000
C	8.779123000	0.922855000	3.358118000
C	24.427554000	4.749043000	3.019933000
H	8.124722000	0.067364000	3.396060000
H	25.283512000	4.094279000	3.030991000
C	10.134507000	0.949014000	3.339684000
C	24.401249000	6.105189000	2.974512000
H	25.231149000	6.791964000	2.940702000
C	10.523351000	2.332202000	3.287302000
C	23.020257000	6.494707000	2.979077000
C	11.837313000	2.772669000	3.255810000
C	22.577380000	7.806194000	2.940632000
C	12.241550000	4.087092000	3.206108000
C	21.255846000	8.200560000	2.944660000
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C	20.811878000	9.566315000	2.903562000
C	13.599719000	5.926885000	3.124311000
C	19.456494000	9.540156000	2.921989000
C	12.198379000	6.303295000	3.131096000
C	19.067651000	8.156971000	2.974453000
C	11.743648000	7.601445000	3.093908000
C	17.753690000	7.716505000	3.005969000
C	10.413680000	7.992053000	3.099649000
C	17.349454000	6.402084000	3.055716000
C	9.971641000	9.359569000	3.059753000
C	15.963757000	5.972472000	3.089574000
H	10.626824000	10.214439000	3.021850000
C	8.616265000	9.334474000	3.079136000
C	15.991284000	4.562291000	3.137515000
H	7.929128000	10.164571000	3.060458000
C	8.225498000	7.952896000	3.130724000
C	17.392625000	4.185881000	3.130732000
C	6.920216000	7.508981000	3.161559000
C	17.847355000	2.887730000	3.167910000
C	6.528340000	6.181632000	3.209959000
C	19.177324000	2.497123000	3.162212000
C	5.163453000	5.740141000	3.242154000
C	19.619364000	1.129609000	3.202140000

H	4.307495000	6.394908000	3.231173000
C	5.189757000	4.383993000	3.287501000
C	20.974741000	1.154706000	3.182845000
H	4.359857000	3.697218000	3.321315000
H	21.661879000	0.324611000	3.201573000
C	6.570747000	3.994472000	3.282845000
C	21.365508000	2.536285000	3.131271000
C	7.013623000	2.682982000	3.321196000
C	22.670791000	2.980203000	3.100506000
H	12.483205000	8.388429000	3.056940000
H	16.984029000	8.474835000	2.989921000
H	6.262337000	1.906204000	3.357389000
H	23.451636000	2.232433000	3.115645000
H	21.466278000	10.421805000	2.865573000
H	18.768662000	10.369638000	2.902278000
Fe	9.386777000	5.141644000	3.208123000
Fe	20.204228000	5.347534000	3.053755000
H	23.328666000	8.582971000	2.904415000
H	6.139371000	8.256753000	3.146490000
C	14.767353000	6.677933000	3.082307000
C	14.823650000	3.811243000	3.179523000
H	12.606973000	2.014338000	3.271829000
H	17.107798000	2.100745000	3.204846000

H	10.822339000	0.119530000	3.359339000
H	18.964180000	0.274737000	3.240006000
H	14.746019000	7.758441000	3.046097000
H	14.844984000	2.730735000	3.215740000

(iv) System 4

70

symmetry c1

N	4.882067000	-2.026543000	-0.000321000
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N	-2.913499000	0.000000000	0.001571000
N	4.882063000	2.026557000	-0.000829000
N	-4.882068000	2.026547000	-0.000222000
N	2.913499000	0.000004000	0.001498000
N	-6.837869000	-0.000005000	-0.001698000
C	5.974623000	-2.851270000	-0.001058000
C	-3.792870000	-2.887767000	0.000471000
C	5.582445000	-4.246926000	-0.001469000
C	-4.222851000	-4.269429000	-0.000268000
H	6.278853000	-5.083364000	-0.002118000
H	-3.552603000	-5.126841000	0.000296000
C	4.222860000	-4.269420000	-0.000777000

C	-5.582435000	-4.246937000	-0.001711000
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C	-5.974616000	-2.851282000	-0.001796000
C	2.481516000	-2.477706000	0.001542000
C	-7.300361000	-2.420984000	-0.002787000
C	2.065728000	-1.143090000	0.002502000
C	-7.690473000	-1.097399000	-0.002606000
C	0.734945000	-0.712821000	0.004335000
C	-9.077626000	-0.678587000	-0.003406000
C	0.734944000	0.712827000	0.004111000
C	-9.077629000	0.678570000	-0.002844000
C	2.065726000	1.143097000	0.002153000
C	-7.690476000	1.097386000	-0.001829000
C	2.481511000	2.477714000	0.000814000
C	-7.300369000	2.420972000	-0.001358000
C	3.792870000	2.887770000	-0.000744000
C	-5.974624000	2.851273000	-0.000718000
C	4.222851000	4.269432000	-0.001962000
C	-5.582447000	4.246930000	-0.000607000
H	3.552603000	5.126844000	-0.002210000
H	-6.278856000	5.083368000	-0.000974000

C	5.582436000	4.246940000	-0.002513000
C	-4.222862000	4.269425000	0.000078000
H	6.278843000	5.083380000	-0.003329000
H	-3.552615000	5.126838000	0.000407000
C	5.974617000	2.851285000	-0.001744000
C	-3.792877000	2.887763000	0.000413000
C	7.300363000	2.420987000	-0.001638000
C	-2.481516000	2.477710000	0.001513000
C	7.690473000	1.097402000	-0.001047000
C	-2.065728000	1.143094000	0.002252000
C	9.077627000	0.678590000	-0.000992000
C	-0.734945000	0.712826000	0.003912000
H	9.925162000	1.361447000	-0.001098000
C	9.077629000	-0.678568000	-0.000813000
C	-0.734944000	-0.712822000	0.004140000
H	9.925165000	-1.361423000	-0.000750000
C	7.690476000	-1.097383000	-0.000814000
C	-2.065726000	-1.143093000	0.002574000
C	7.300368000	-2.420970000	-0.001100000
C	-2.481511000	-2.477710000	0.002001000
H	1.699908000	3.238822000	0.001143000
H	-8.082124000	3.182060000	-0.001622000
H	8.082122000	-3.182057000	-0.001359000

H	-1.699909000	-3.238818000	0.002850000
H	-9.925161000	-1.361444000	-0.004235000
H	-9.925165000	1.361426000	-0.003118000
Fe	4.842045000	0.000006000	-0.000289000
Fe	-4.842045000	-0.000002000	-0.000413000
H	-8.082114000	-3.182074000	-0.003656000
H	8.082116000	3.182077000	-0.002058000
H	1.699915000	-3.238815000	0.002118000
H	-1.699916000	3.238820000	0.002056000