Can heterometallic 1-dimensional chains support current rectification?

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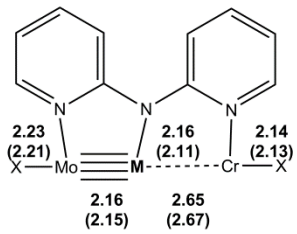
Supporting information.

Computational methods

All calculations of gas-phase electronic structure were performed using the Amsterdam Density Functional package ADF2012[1] package and the BP86 functional.[2] A double-ζ Slater-type basis set, extended with a single polarization function, was used to describe the main group atoms, while cobalt was modeled with a triple-ζ basis set. Electrons in orbitals up to and including 1s {C, N}, 2p{Cl}, 3p {Cr, Mn, Co} and 4p {Mo} were considered part of the core and treated in accordance with the frozen core approximation. The local density approximation was employed for the optimizations,[3] along with the local exchange-correlation potential of Vosko, Wilk and Nusair[4] and gradient corrections to exchange and correlation proposed by Becke and Perdew (BP86).[5] Different configurations were defined using the 'occupations' key. All structures were optimized using the gradient algorithm of Versluis and Ziegler.[6] Transport calculations were performed with ATK11.2.3[7,8] package using the gradient corrected PBE functional.[9] The methodology combines a density functional theory treatment of the electronic structure with the Keldysh non-equilibrium Green's function approach to simulating coherent transport.[10] All atoms were treated with double-ζ basis set, extended with single polarization function. Core electrons were described by norm-conserving pseudopotentials.[11] The electronic structure of the two-probe systems at equilibrium was converged using a 100 Ry mesh cut-off, finite temperature of 300K at the electrodes, and the real space density constraint at the electrodes. Sampling of the Brillouin zone was performed using a Monkhorst-Pack grid[12] with 300 k-points along the transport direction. In the calculation of the transmission spectra and currents, a 5 x 5 grid was used to sample the Brillouin zone, and the bias window was sampled

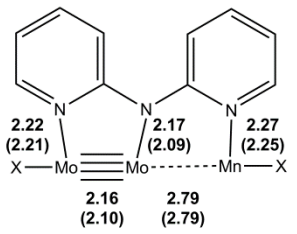
at 0.01 eV intervals. The initial spin density for the two-probe calculations was polarized to be consistent with the net spin densities of the isolated molecules in their gas phase ground states. The scattering region contained the EMAC sandwiched between 4 x 4 layer of the Au (111) surface of the source and the drain, respectively. The sulphur atoms of the two NCS^- ligands are located in a hollow site on the Au (111) surface with Au-S distance 2.52 Å. The precise details of the contact geometry remain a significant issue in all transport calculations – the 'hollow-site' geometry with a gold-sulfur distance of 2.52 Å (corresponding to a distance of ~1.9 Å between the sulfur and the surface) adopted here has been established as the global minimum for many examples of sulfur coordination to Au (111)[13] and is used in the majority of comparative studies.[14] The transmission spectra are not influenced strongly by alternative choices of contact geometry.

Figure S1 Comparison of optimised and X-ray crystallographic structural parameters.

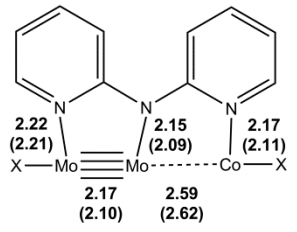


$^5B_1$

Note X-ray data corresponds to MoWCr while computation relates to Mo_2Cr.



$^6A_1$



^4E

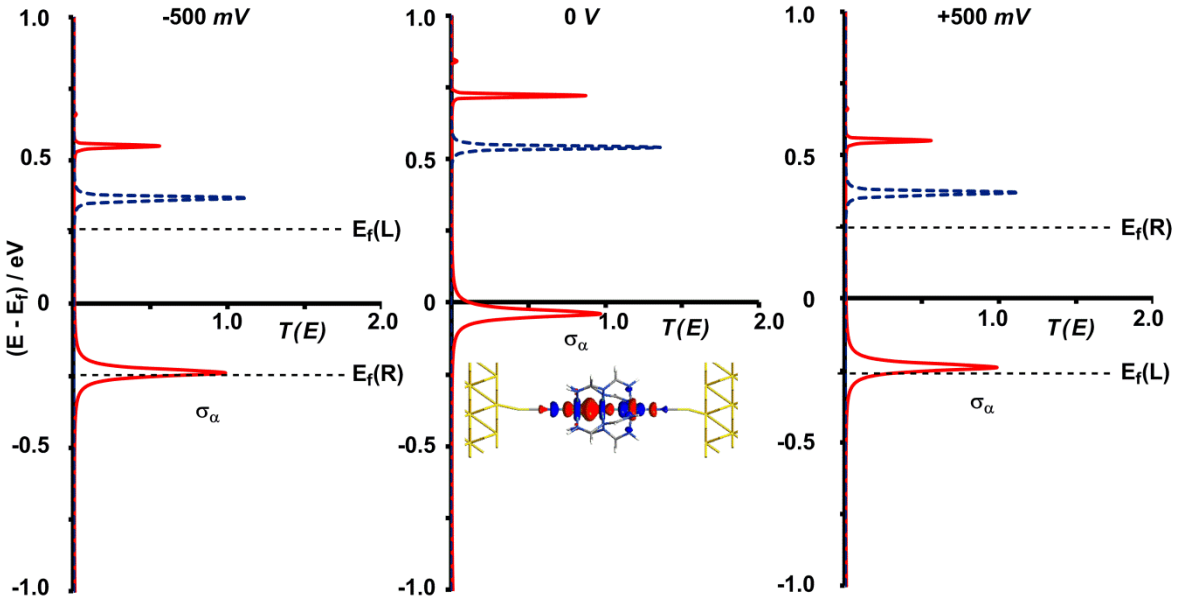


Figure S2 Bias-dependence of the transmission spectra for Mo_2Cr.

Optimised Cartesian coordinates and total energies of Mo_2Cr, Mo_2Mn and Mo_2Co.

$Mo_2Cr(dpa)_4(NCS)_2$ $^5B_1$ E=-644.90 eV

S	0.000000000	0.000000000	-7.404126000
S	0.000000000	0.000000000	7.447030000
C	0.000000000	0.000000000	-5.791980000
C	0.000000000	0.000000000	5.836557000
N	0.000000000	0.000000000	-4.591682000
N	0.000000000	0.000000000	4.637168000
Mo	0.000000000	0.000000000	-2.272369000
Mo	0.000000000	0.000000000	-0.111881000
Cr	0.000000000	0.000000000	2.542077000
N	-1.147116000	-1.908201000	-2.243923000
N	-1.907213000	1.147086000	-2.245245000
N	1.907213000	-1.147086000	-2.245245000
N	1.147116000	1.908201000	-2.243923000
N	-1.626318000	1.406242000	0.048946000
N	-1.405348000	-1.626771000	0.050303000
N	1.626318000	-1.406242000	0.048946000
N	1.405348000	1.626771000	0.050303000
N	-1.828197000	-1.088703000	2.286798000
N	1.092319000	-1.828076000	2.286609000
N	-1.092319000	1.828076000	2.286609000
N	1.828197000	1.088703000	2.286798000
C	-1.290019000	-2.647036000	-3.371103000
C	-1.806328000	-3.928233000	-3.377444000
C	-2.158539000	-4.509147000	-2.153443000
C	-2.034719000	-3.766904000	-0.994064000
C	-1.569606000	-2.439097000	-1.051046000
C	-2.258435000	-1.674238000	1.125348000
C	-3.575407000	-2.181727000	1.051316000
C	-4.401951000	-2.148570000	2.156085000
C	-3.931896000	-1.594795000	3.350130000
C	-2.656061000	-1.063952000	3.355870000

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H	-4.543596000	-1.551416000	4.250547000
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C	2.437709000	-1.571396000	-1.052897000
C	1.673987000	-2.259540000	1.123782000
C	2.176863000	-3.578103000	1.047577000
C	2.143994000	-4.404832000	2.152093000
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C	4.401951000	2.148570000	2.156085000
C	3.575407000	2.181727000	1.051316000
C	2.258435000	1.674238000	1.125348000
C	1.569606000	2.439097000	-1.051046000
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H	4.543596000	1.551416000	4.250547000
H	2.244525000	0.590417000	4.247065000
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C	-2.437709000	1.571396000	-1.052897000
C	-1.673987000	2.259540000	1.123782000
C	-2.176863000	3.578103000	1.047577000
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C	-1.596426000	3.932879000	3.348272000
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H	-1.554157000	4.544518000	4.248701000
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H	-2.525181000	5.424961000	2.076221000
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H	2.507127000	5.542179000	-2.105307000
H	-5.420627000	-2.534154000	2.081920000
H	-2.507127000	-5.542179000	-2.105307000
H	5.420627000	2.534154000	2.081920000

$Mo_2Mn(dpa)_4(NCS)_2$ $^6A_1$ E=-644.99 eV

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N	0.000000000	0.000000000	4.746522000
Mo	0.000000000	0.000000000	-2.208579000
Mo	0.000000000	0.000000000	-0.047122000
Mn	0.000000000	0.000000000	2.745753000
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N	-1.909425000	1.128854000	-2.210193000
N	1.909425000	-1.128854000	-2.210193000
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N	1.633896000	-1.414820000	0.082662000
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N	-1.182620000	1.896342000	2.321332000
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C	-1.820179000	-3.909884000	-3.360670000
C	-2.203339000	-4.486571000	-2.143478000
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C	-4.051433000	-1.641090000	3.293509000
C	-2.751225000	-1.172392000	3.361541000
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C	4.483372000	-2.210427000	-2.144054000
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C	2.434047000	-1.577600000	-1.025603000
C	1.682945000	-2.314063000	1.126691000
C	2.116142000	-3.650638000	0.975876000
C	2.102176000	-4.509370000	2.057351000
C	1.642778000	-4.051322000	3.295020000
C	1.174681000	-2.750834000	3.363169000
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H	1.621146000	-4.690150000	4.177200000
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H	4.183435000	-2.334915000	-0.014289000

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H	2.163716000	-0.910180000	-4.250421000
C	2.751225000	1.172392000	3.361541000
C	4.051433000	1.641090000	3.293509000
C	4.507812000	2.104926000	2.056723000
C	3.648050000	2.121299000	0.975951000
C	2.312242000	1.685314000	1.126352000
C	1.574893000	2.435355000	-1.026121000
C	2.074150000	3.752399000	-0.980832000
C	2.203339000	4.486571000	-2.143478000
C	1.820179000	3.909884000	-3.360670000
C	1.272165000	2.642798000	-3.342907000
H	0.909297000	2.164660000	-4.251420000
H	1.909865000	4.446562000	-4.304824000
H	2.327680000	4.186100000	-0.013724000
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H	4.691120000	1.617082000	4.175093000
H	2.351759000	0.761009000	4.289975000
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C	-2.434047000	1.577600000	-1.025603000
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C	-2.116142000	3.650638000	0.975876000
C	-2.102176000	4.509370000	2.057351000
C	-1.642778000	4.051322000	3.295020000
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H	-0.765434000	2.350427000	4.292125000
H	-1.621146000	4.690150000	4.177200000
H	-2.424801000	4.006377000	-0.006282000
H	-4.183435000	2.334915000	-0.014289000
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H	2.429673000	-5.543205000	1.931584000
H	-2.429673000	5.543205000	1.931584000
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H	2.579547000	5.510277000	-2.104586000
H	-5.541172000	-2.433932000	1.931015000
H	-2.579547000	-5.510277000	-2.104586000
H	5.541172000	2.433932000	1.931015000

$Mo_2Co(dpa)_4(NCS)_2$ ^4E E=-642.72 eV

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N	0.000000000	0.000000000	-4.470100000
N	0.000000000	0.000000000	4.472429000
Mo	0.000000000	0.000000000	-2.228237000
Mo	0.000000000	0.000000000	-0.060879000
Co	0.000000000	0.000000000	2.528276000
N	-1.120801000	-1.916444000	-2.215646000
N	-1.926129000	1.101225000	-2.220788000
N	1.926129000	-1.101225000	-2.220788000
N	1.120801000	1.916444000	-2.215646000

N	-1.620068000	1.415031000	0.060419000
N	-1.420789000	-1.613240000	0.068253000
N	1.620068000	-1.415031000	0.060419000
N	1.420789000	1.613240000	0.068253000
N	-1.878451000	-1.063379000	2.282621000
N	1.076865000	-1.872484000	2.277129000
N	-1.076865000	1.872484000	2.277129000
N	1.878451000	1.063379000	2.282621000
C	-1.256593000	-2.664043000	-3.338806000
C	-1.803516000	-3.931807000	-3.345157000
C	-2.197439000	-4.493055000	-2.123786000
C	-2.078614000	-3.744158000	-0.969401000
C	-1.577461000	-2.428433000	-1.026843000
C	-2.306636000	-1.636357000	1.124114000
C	-3.635980000	-2.099271000	1.013069000
C	-4.484777000	-2.032797000	2.100814000
C	-4.019776000	-1.488309000	3.300133000
C	-2.725025000	-0.999571000	3.328122000
H	-0.886429000	-2.199285000	-4.251071000
H	-1.884176000	-4.480944000	-4.282990000
H	-2.336889000	-4.166284000	0.001483000
H	-3.996461000	-2.468304000	0.053985000
H	-4.650219000	-1.417278000	4.185963000
H	-2.323275000	-0.526143000	4.223232000
C	2.685571000	-1.207405000	-3.338896000
C	3.971443000	-1.710919000	-3.338480000
C	4.536409000	-2.093742000	-2.115587000
C	3.774851000	-2.008167000	-0.966548000
C	2.444529000	-1.547998000	-1.030600000
C	1.669733000	-2.289810000	1.124223000
C	2.176296000	-3.604634000	1.026278000
C	2.129433000	-4.448069000	2.119184000
C	1.559840000	-3.993785000	3.311030000
C	1.031116000	-2.714658000	3.327115000
H	0.539363000	-2.322419000	4.216589000
H	1.501406000	-4.620700000	4.200244000
H	2.564051000	-3.959587000	0.072509000
H	4.198649000	-2.258000000	0.005823000
H	4.530117000	-1.767274000	-4.272273000
H	2.215552000	-0.847943000	-4.252704000
C	2.725025000	0.999571000	3.328122000
C	4.019776000	1.488309000	3.300133000
C	4.484777000	2.032797000	2.100814000
C	3.635980000	2.099271000	1.013069000
C	2.306636000	1.636357000	1.124114000
C	1.577461000	2.428433000	-1.026843000
C	2.078614000	3.744158000	-0.969401000
C	2.197439000	4.493055000	-2.123786000
C	1.803516000	3.931807000	-3.345157000
C	1.256593000	2.664043000	-3.338806000
H	0.886429000	2.199285000	-4.251071000
H	1.884176000	4.480944000	-4.282990000
H	2.336889000	4.166284000	0.001483000
H	3.996461000	2.468304000	0.053985000
H	4.650219000	1.417278000	4.185963000
H	2.323275000	0.526143000	4.223232000
C	-2.685571000	1.207405000	-3.338896000
C	-3.971443000	1.710919000	-3.338480000

C	-4.536409000	2.093742000	-2.115587000
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C	-2.444529000	1.547998000	-1.030600000
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C	-1.031116000	2.714658000	3.327115000
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H	-1.501406000	4.620700000	4.200244000
H	-2.564051000	3.959587000	0.072509000
H	-4.198649000	2.258000000	0.005823000
H	-4.530117000	1.767274000	-4.272273000
H	-2.215552000	0.847943000	-4.252704000
H	5.571900000	-2.433950000	-2.060962000
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H	-2.514396000	5.466153000	2.035553000
H	-5.571900000	2.433950000	-2.060962000
H	2.573261000	5.516461000	-2.074781000
H	-5.514352000	-2.383432000	2.007753000
H	-2.573261000	-5.516461000	-2.074781000
H	5.514352000	2.383432000	2.007753000

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