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In search of structure-function relationships in transition-metal based rectifiers: the influence of spin polarisation.

Tingting Weng, Daniel DeBrincat, Vaida Arcisauskaite and John E. McGrady

Supporting Information

1. Structure and stability of the low-lying spin states of $Ru_2Ni(dpa)_4(NCS)_2$ and $Ru_2Cu(dpa)_4(NCS)_2$ in the gas phase.

As described in the text, the electronic structure of these chains is best described as $\{Ru_2\}^{5+}M^+$. The local spin moment on the $\{Ru_2\}^{5+}$ unit is 3/2, that on Ni^+ is S = 1/2 and Cu^+ is diamagnetic. For $Ru_2Cu(dpa)_4(NCS)_2$ there is therefore only a single low-lying spin state, S_{tot}=3/2. For $Ru_2Ni(dpa)_4(NCS)_2$ there are two states, S_{tot}=2 and S_{tot}=1, corresponding to ferro- and antiferromagnetic coupling between the subunits, respectively. Relative energies of these spin states and their optimised Cartesian coordinates are presented below. In the $Ru_2Ni(dpa)_4(NCS)_2$ case the ferromagnetic S_{tot}=2 state is most stable, indicating that ferromagnetic coupling prevails: this is to be expected as the Ni SOMO, the $d_{x^2-y^2}$ orbital, is approximately orthogonal to all three SOMOs on $\{Ru_2\}$ (π_{xz},π_{yz},δ} . The optimised structural parameters of the two states are almost identical.

Table S1 Optimised coordinates of $Ru_2Ni(dpa)_4(NCS)_2$

S_{tot}=2 (E_{rel} = 0 ev)

Ru	0.000000	0.000000	2.253911
Ru	0.000000	0.000000	-0.112716
Ni	0.000000	0.000000	-2.538490
N	2.092655	-0.273966	2.141182
N	2.020053	0.382590	-0.096116
N	1.844897	1.029799	-2.318059
N	0.273362	2.092707	2.141459
N	-0.382665	2.020038	-0.096004
N	-1.030292	1.844711	-2.317782
N	-2.092655	0.273966	2.141182
N	-2.020053	-0.382590	-0.096116
N	-1.844897	-1.029799	-2.318059
N	-0.273362	-2.092707	2.141459
N	0.382665	-2.020038	-0.096004
N	1.030292	-1.844711	-2.317782
C	2.771621	-0.757696	3.206641
H	2.175838	-0.895600	4.106418
C	4.120234	-1.056572	3.175046
H	4.609439	-1.437307	4.070653
C	4.809693	-0.886415	1.970077
H	5.863050	-1.158691	1.886403
C	4.135992	-0.397740	0.869396
H	4.634315	-0.307297	-0.094901
C	2.769186	-0.060785	0.961983
C	2.548065	1.088778	-1.154430
C	3.676726	1.925069	-1.044160
H	4.173636	2.029612	-0.080450
C	4.107426	2.644151	-2.143837
H	4.975009	3.300671	-2.057694
C	3.406146	2.541104	-3.346978
H	3.710994	3.085003	-4.240469
C	2.274455	1.741819	-3.375761

H	1.666341	1.641348	-4.275386
C	0.756153	2.771960	3.207175
H	0.894821	2.176066	4.106754
C	1.053085	4.121008	3.176086
H	1.433093	4.610418	4.071890
C	0.881941	4.810705	1.971385
H	1.152607	5.864510	1.888163
C	0.394380	4.136692	0.870406
H	0.303254	4.635230	-0.093716
C	0.059446	2.769345	0.962473
C	-1.090057	2.547370	-1.153875
C	-1.928163	3.674605	-1.042934
H	-2.033262	4.170968	-0.078999
C	-2.648275	4.104530	-2.142245
H	-3.306240	4.970966	-2.055566
C	-2.544364	3.403927	-3.345702
H	-3.088977	3.708255	-4.238935
C	-1.743241	2.273547	-3.375140
H	-1.642059	1.665911	-4.275014
C	-2.771621	0.757696	3.206641
H	-2.175838	0.895600	4.106418
C	-4.120234	1.056572	3.175046
H	-4.609439	1.437307	4.070653
C	-4.809693	0.886415	1.970077
H	-5.863050	1.158691	1.886403
C	-4.135992	0.397740	0.869396
H	-4.634315	0.307297	-0.094901
C	-2.769186	0.060785	0.961983
C	-2.548065	-1.088778	-1.154430
C	-3.676726	-1.925069	-1.044160
H	-4.173636	-2.029612	-0.080450
C	-4.107426	-2.644151	-2.143837
H	-4.975009	-3.300671	-2.057694
C	-3.406146	-2.541104	-3.346978
H	-3.710994	-3.085003	-4.240469
C	-2.274455	-1.741819	-3.375761
H	-1.666341	-1.641348	-4.275386
C	-0.756153	-2.771960	3.207175
H	-0.894821	-2.176066	4.106754
C	-1.053085	-4.121008	3.176086
H	-1.433093	-4.610418	4.071890
C	-0.881941	-4.810705	1.971385
H	-1.152607	-5.864510	1.888163
C	-0.394380	-4.136692	0.870406
H	-0.303254	-4.635230	-0.093716
C	-0.059446	-2.769345	0.962473
C	1.090057	-2.547370	-1.153875
C	1.928163	-3.674605	-1.042934
H	2.033262	-4.170968	-0.078999
C	2.648275	-4.104530	-2.142245
H	3.306240	-4.970966	-2.055566
C	2.544364	-3.403927	-3.345702
H	3.088977	-3.708255	-4.238935
C	1.743241	-2.273547	-3.375140
H	1.642059	-1.665911	-4.275014
N	0.000000	0.000000	4.406359
C	0.000000	0.000000	5.606580
S	0.000000	0.000000	7.221941
N	0.000000	0.000000	-4.586071
C	0.000000	0.000000	-5.781586
S	0.000000	0.000000	-7.401590

S_{tot}=1 (E_{rel} = 0.10 ev)

Ru	0.000000	0.000000	2.260071
Ru	0.000000	0.000000	-0.097234
Ni	0.000000	0.000000	-2.543455
N	2.096896	-0.276237	2.144031
N	2.021498	0.359701	-0.098947
N	1.856591	0.981606	-2.332906
N	0.275579	2.096963	2.144279
N	-0.359741	2.021549	-0.098893
N	-0.982092	1.856485	-2.332664
N	-2.096896	0.276237	2.144031
N	-2.021498	-0.359701	-0.098947
N	-1.856591	-0.981606	-2.332906
N	-0.275579	-2.096963	2.144279
N	0.359741	-2.021549	-0.098893
N	0.982092	-1.856485	-2.332664
C	2.778152	-0.747579	3.213419
H	2.182793	-0.883219	4.113920
C	4.128920	-1.036946	3.185026
H	4.620064	-1.408005	4.083587
C	4.818395	-0.869195	1.979470
H	5.874173	-1.133024	1.899109
C	4.142304	-0.394407	0.874481
H	4.640944	-0.304900	-0.089803
C	2.772070	-0.068549	0.962907
C	2.544918	1.064637	-1.161226
C	3.655992	1.922786	-1.044839
H	4.134614	2.048147	-0.074150
C	4.093684	2.633338	-2.147353
H	4.950364	3.303501	-2.057380
C	3.410562	2.504384	-3.358153
H	3.721974	3.037611	-4.255860
C	2.289518	1.690447	-3.391980
H	1.693376	1.571999	-4.297324
C	0.745853	2.778498	3.213972
H	0.882254	2.183014	4.114270
C	1.033173	4.129703	3.186133
H	1.403434	4.621040	4.084919
C	0.864442	4.819428	1.980861
H	1.126599	5.875655	1.900976
C	0.390867	4.143035	0.875539
H	0.300677	4.641907	-0.088560
C	0.067118	2.772275	0.963396
C	-1.065889	2.544271	-1.160717
C	-1.925767	3.653925	-1.043713
H	-2.051696	4.131968	-0.072809
C	-2.637197	4.090956	-2.145927
H	-3.308711	4.946532	-2.055470
C	-2.507359	3.408585	-3.357039
H	-3.041193	3.719584	-4.254531
C	-1.691725	2.288780	-3.391452
H	-1.572618	1.693105	-4.297022
C	-2.778152	0.747579	3.213419
H	-2.182793	0.883219	4.113920
C	-4.128920	1.036946	3.185026
H	-4.620064	1.408005	4.083587
C	-4.818395	0.869195	1.979470
H	-5.874173	1.133024	1.899109
C	-4.142304	0.394407	0.874481
H	-4.640944	0.304900	-0.089803
C	-2.772070	0.068549	0.962907
C	-2.544918	-1.064637	-1.161226
C	-3.655992	-1.922786	-1.044839
H	-4.134614	-2.048147	-0.074150
C	-4.093684	-2.633338	-2.147353
H	-4.950364	-3.303501	-2.057380

C	-3.410562	-2.504384	-3.358153
H	-3.721974	-3.037611	-4.255860
C	-2.289518	-1.690447	-3.391980
H	-1.693376	-1.571999	-4.297324
C	-0.745853	-2.778498	3.213972
H	-0.882254	-2.183014	4.114270
C	-1.033173	-4.129703	3.186133
H	-1.403434	-4.621040	4.084919
C	-0.864442	-4.819428	1.980861
H	-1.126599	-5.875655	1.900976
C	-0.390867	-4.143035	0.875539
H	-0.300677	-4.641907	-0.088560
C	-0.067118	-2.772275	0.963396
C	1.065889	-2.544271	-1.160717
C	1.925767	-3.653925	-1.043713
H	2.051696	-4.131968	-0.072809
C	2.637197	-4.090956	-2.145927
H	3.308711	-4.946532	-2.055470
C	2.507359	-3.408585	-3.357039
H	3.041193	-3.719584	-4.254531
C	1.691725	-2.288780	-3.391452
H	1.572618	-1.693105	-4.297022
N	0.000000	0.000000	4.428487
C	0.000000	0.000000	5.628988
S	0.000000	0.000000	7.243383
N	0.000000	0.000000	-4.594759
C	0.000000	0.000000	-5.790078
S	0.000000	0.000000	-7.411351

Table S1 Optimised coordinates of bent $Ru_2Ni(dpa)_4(NCS)_2$

S_{tot}=2 (E_{rel} = -0.05 ev)

Ru	0.034264	0.028642	2.253214
Ru	-0.066977	-0.084777	-0.118148
Ni	0.030471	0.045218	-2.543317
N	2.102747	-0.258031	2.134077
N	1.975693	0.333120	-0.124554
N	1.821223	1.042846	-2.334199
N	0.320454	2.087344	2.109003
N	-0.411320	1.965388	-0.105060
N	-1.040739	1.827568	-2.338471
N	-2.078387	0.305317	2.150002
N	-2.065272	-0.430746	-0.062778
N	-1.879976	-1.050138	-2.286202
N	-0.245885	-2.094426	2.162579
N	0.351167	-2.073227	-0.093855
N	1.038347	-1.851972	-2.297682
C	2.804787	-0.713698	3.198004
H	2.228082	-0.825389	4.113976
C	4.151507	-1.014604	3.141787
H	4.662702	-1.369785	4.035678
C	4.811881	-0.879678	1.915346
H	5.863036	-1.154726	1.814714
C	4.111123	-0.424362	0.817330
H	4.585785	-0.359315	-0.161217
C	2.747303	-0.081103	0.931922
C	2.499515	1.079875	-1.154655
C	3.609811	1.938792	-1.009101
H	4.091229	2.029788	-0.036147
C	4.043827	2.691965	-2.083001
H	4.895822	3.363779	-1.965054
C	3.367882	2.604040	-3.303243
H	3.679601	3.173841	-4.177892
C	2.253684	1.785288	-3.370143

H	1.661139	1.689962	-4.281044
C	0.847396	2.782487	3.143953
H	0.996760	2.204994	4.054297
C	1.168157	4.123354	3.067463
H	1.581557	4.630931	3.937981
C	0.975088	4.782667	1.847842
H	1.263492	5.828183	1.727858
C	0.441834	4.090562	0.780085
H	0.330958	4.567117	-0.193164
C	0.080069	2.732445	0.916932
C	-1.109542	2.507534	-1.161941
C	-1.952529	3.630092	-1.038447
H	-2.057915	4.113340	-0.067635
C	-2.673208	4.071743	-2.132269
H	-3.335097	4.934053	-2.035012
C	-2.566799	3.386567	-3.345020
H	-3.115064	3.698247	-4.233473
C	-1.757484	2.263533	-3.391097
H	-1.651933	1.669461	-4.299047
C	-2.732588	0.834948	3.208641
H	-2.119679	1.003803	4.090818
C	-4.079244	1.145802	3.195736
H	-4.543936	1.565301	4.087060
C	-4.797052	0.937265	2.014325
H	-5.849600	1.216019	1.943083
C	-4.151747	0.399955	0.919183
H	-4.671551	0.279332	-0.030088
C	-2.786435	0.055761	0.995449
C	-2.603823	-1.109638	-1.135538
C	-3.750676	-1.920450	-1.047055
H	-4.266522	-2.018868	-0.092693
C	-4.173388	-2.628258	-2.158272
H	-5.055243	-3.267848	-2.091816
C	-3.445917	-2.536090	-3.345571
H	-3.741114	-3.074383	-4.245734
C	-2.300688	-1.753344	-3.351546
H	-1.677922	-1.664035	-4.241696
C	-0.701884	-2.758525	3.249128
H	-0.846523	-2.147202	4.136124
C	-0.969411	-4.115015	3.259285
H	-1.330105	-4.585068	4.173348
C	-0.793801	-4.835971	2.075353
H	-1.037448	-5.898400	2.025655
C	-0.338964	-4.179162	0.949527
H	-0.249653	-4.699807	-0.002931
C	-0.041089	-2.803006	1.000557
C	1.083762	-2.577029	-1.144931
C	1.929237	-3.699413	-1.040670
H	2.026392	-4.211119	-0.084240
C	2.668967	-4.104739	-2.136329
H	3.332631	-4.967256	-2.053838
C	2.575370	-3.386904	-3.330085
H	3.133340	-3.673817	-4.220786
C	1.767175	-2.260918	-3.351294
H	1.674354	-1.640051	-4.243086
N	0.003563	0.009168	4.370882
C	-0.105092	-0.073450	5.562972
S	-0.243400	-0.174993	7.169387
N	-0.004325	-0.020413	-4.557146
C	-0.150189	-0.092489	-5.740934
S	-0.347807	-0.181555	-7.345641

Table S1 Optimised coordinates of $Ru_2Cu(dpa)_4(NCS)_2$

S_{tot}=3/2 (E_{rel} = 0 ev) (only accessible state as Cu^+ is diamagnetic)

Ru	0.000000	0.000000	-2.195172
Ru	0.000000	0.000000	0.152430
Cu	0.000000	0.000000	2.731420
N	-1.783008	1.283046	2.347242
N	-1.228236	1.657693	0.123853
N	-0.639793	2.014161	-2.103193
N	-1.282954	-1.782253	2.347456
N	-1.657854	-1.227956	0.123989
N	-2.014359	-0.639304	-2.102994
N	1.783008	-1.283046	2.347242
N	1.228236	-1.657693	0.123853
N	0.639793	-2.014161	-2.103193
N	1.282954	1.782253	2.347456
N	1.657854	1.227956	0.123989
N	2.014359	0.639304	-2.102994
C	-2.651550	1.340203	3.369352
H	-2.294979	0.901783	4.303593
C	-3.908680	1.918317	3.270602
H	-4.563946	1.956778	4.140314
C	-4.303932	2.415767	2.027086
H	-5.302274	2.833422	1.885052
C	-3.426700	2.351327	0.959154
H	-3.730279	2.682309	-0.034090
C	-2.144111	1.802280	1.148683
C	-1.162794	2.519260	-0.934944
C	-1.511792	3.885511	-0.860788
H	-1.852794	4.287045	0.092691
C	-1.371980	4.700789	-1.964507
H	-1.630958	5.758618	-1.895351
C	-0.866260	4.165935	-3.154550
H	-0.735134	4.772211	-4.049868
C	-0.498803	2.834178	-3.169656
H	-0.078622	2.368862	-4.058292
C	-1.341093	-2.650227	3.370026
H	-0.901535	-2.293995	4.303850
C	-1.921563	-3.906330	3.272196
H	-1.960665	-4.561119	4.142238
C	-2.420615	-4.301207	2.029207
H	-2.840265	-5.298817	1.887920
C	-2.355228	-3.424600	0.960840
H	-2.687416	-3.728031	-0.032039
C	-1.803595	-2.142959	1.149365
C	-2.519787	-1.161402	-0.934462
C	-3.886559	-1.508196	-0.859707
H	-4.288330	-1.848133	0.094054
C	-4.701957	-1.367682	-1.963257
H	-5.760163	-1.625001	-1.893642
C	-4.166710	-0.863349	-3.153706
H	-4.773033	-0.731821	-4.048934
C	-2.834454	-0.497692	-3.169306
H	-2.368830	-0.078382	-4.058194
C	2.651550	-1.340203	3.369352
H	2.294979	-0.901783	4.303593
C	3.908680	-1.918317	3.270602
H	4.563946	-1.956778	4.140314
C	4.303932	-2.415767	2.027086
H	5.302274	-2.833422	1.885052
C	3.426700	-2.351327	0.959154
H	3.730279	-2.682309	-0.034090
C	2.144111	-1.802280	1.148683
C	1.162794	-2.519260	-0.934944
C	1.511792	-3.885511	-0.860788

H	1.852794	-4.287045	0.092691
C	1.371980	-4.700789	-1.964507
H	1.630958	-5.758618	-1.895351
C	0.866260	-4.165935	-3.154550
H	0.735134	-4.772211	-4.049868
C	0.498803	-2.834178	-3.169656
H	0.078622	-2.368862	-4.058292
C	1.341093	2.650227	3.370026
H	0.901535	2.293995	4.303850
C	1.921563	3.906330	3.272196
H	1.960665	4.561119	4.142238
C	2.420615	4.301207	2.029207
H	2.840265	5.298817	1.887920
C	2.355228	3.424600	0.960840
H	2.687416	3.728031	-0.032039
C	1.803595	2.142959	1.149365
C	2.519787	1.161402	-0.934462
C	3.886559	1.508196	-0.859707
H	4.288330	1.848133	0.094054
C	4.701957	1.367682	-1.963257
H	5.760163	1.625001	-1.893642
C	4.166710	0.863349	-3.153706
H	4.773033	0.731821	-4.048934
C	2.834454	0.497692	-3.169306
H	2.368830	0.078382	-4.058194
N	0.000000	0.000000	-4.305466
C	0.000000	0.000000	-5.505724
S	0.000000	0.000000	-7.118103
N	0.000000	0.000000	4.698600
C	0.000000	0.000000	5.892232
S	0.000000	0.000000	7.512159

2. The **eigenvalues of the projected self-consistent Hamiltonian** are complementary to the transmission peaks: there is an approximate 1:1 correspondence between the positions of the peaks and the eigenvalues, although channels of δ symmetry do not appear in the transmission due to weak coupling with the surface. In Figure S1 the key feature is that the spin-β π^* channel enters the bias window only under forward bias while the spin-α π^* channel enters only under reverse bias.

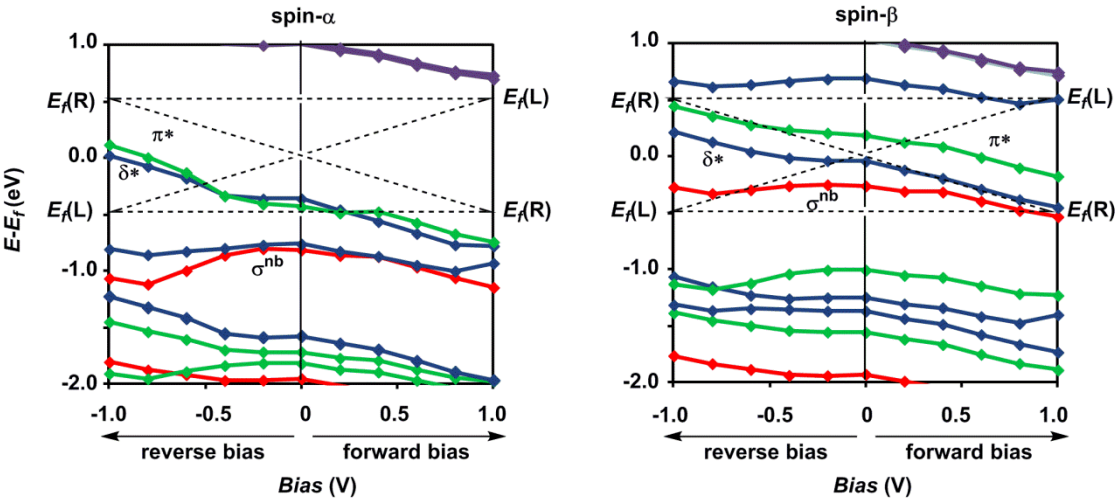

Figure S1 Eigenvalues of the Molecular Projected Self-Consistent Hamiltonian (MPSH) for $Ru_2Ni(dpa)_4(NCS)_2$ under forward and reverse bias.

3. Dependence of transmission spectra on functional

The transmission spectra shown in the text are computed using the LDA functional with the Perdew-Zunger correction for self interaction. Figure S2 shows the corresponding figure for $Ru_2Ni(dpa)_4(NCS)_2$ computed using the PBE functional. The key features are identical to those in the main text: the distinction between the spin-α and spin-β components of π^* is maintained, although the PBE functional imposes a marginally greater separation between the two. As a result, the spin-α π^* and σ^{nb} peaks merge in the PBE transmission (the presence of a shoulder in the feature at -0.7 eV confirms the contribution of two distinct bands).

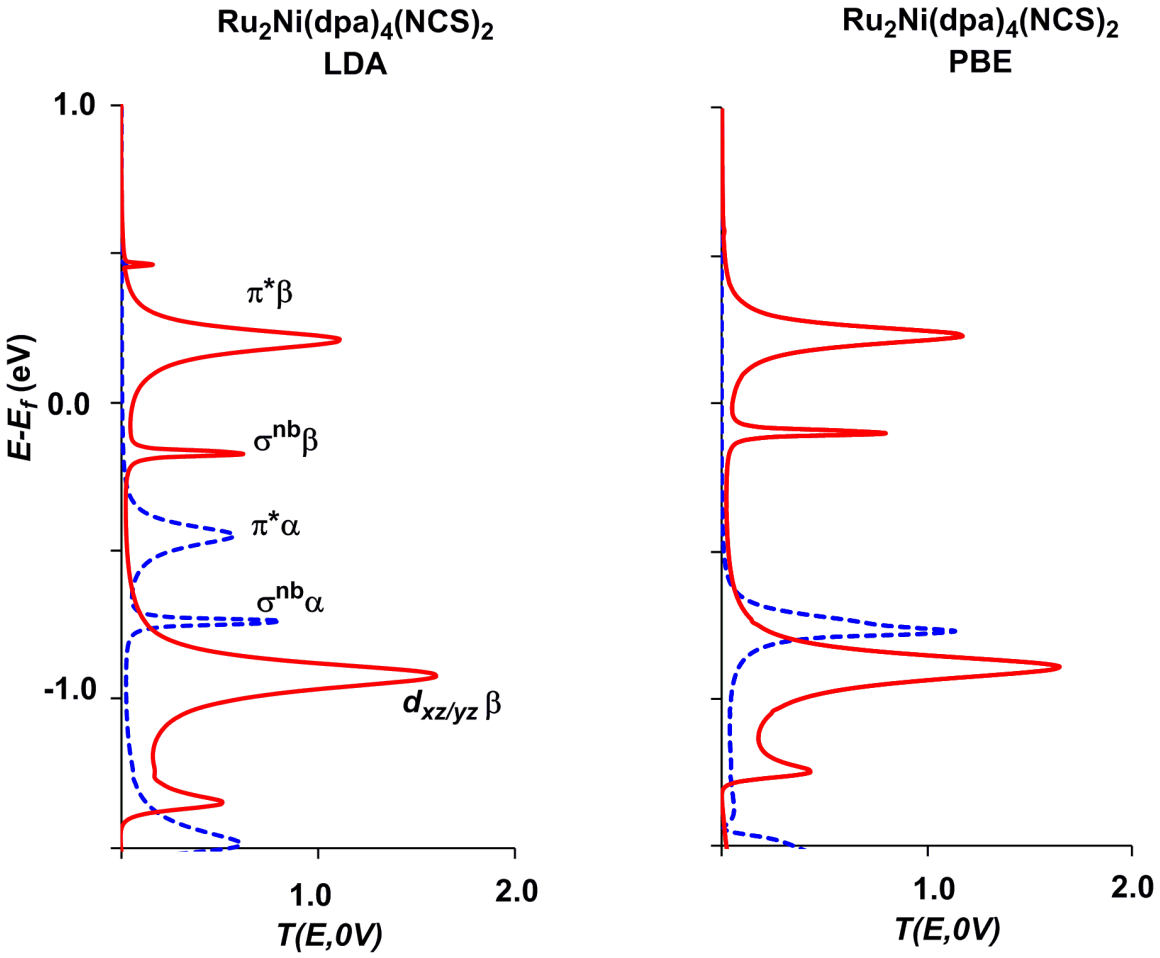

Figure S2 Zero-bias transmission spectrum of $Ru_2Ni(dpa)_4(NCS)_2$ using the LDA and PBE functionals.

4. Dependence of transmission spectra on structure

In the main text it was noted that the linear geometry for $Ru_2Ni(dpa)_4(NCS)_2$ does not correspond to a minimum on the potential energy surface – a slight bending is driven by a second-order Jahn-Teller instability. The transmission spectra shown below for linear and bent geometries shows that the effect of bending is marginal: the π^* peaks separate into two distinct components (their degeneracy is lifted by the distortion) but otherwise the key features are the same.

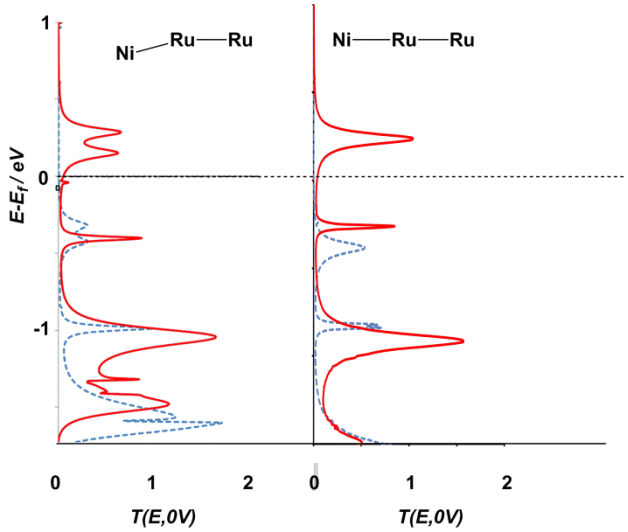

Figure S3 Zero-bias transmission spectra of linear and bent $Ru_2Ni(dpa)_4(NCS)_2$ (LDA+PZ functional).