Supplementary Information

Pressure-Induced Metallicity and Piezoreductive Transition of Metal-Centers in Conductive 2-Dimensional Metal-Organic Frameworks

Khoa N. Le[a] and Christopher H. Hendon*[a]

[a.] Department of Chemistry and Biochemistry, University of Oregon, Eugene, OR, 97401, USA.

Bond lengths for the monolayers:

Table 1. $Ni_3(HIB)_2$ bond lengths at different hydrostatic pressure.

Pressure (kB)	Bond Length (Å)			
	Ni-N	N-C	N-H	C-C
42.83	1.72895	1.29975	1.01484	1.34831
39.67	1.73125	1.30184	1.01541	1.35169
36.68	1.73366	1.30396	1.01593	1.35509
33.78	1.73639	1.30614	1.01644	1.35846
31.04	1.73938	1.30815	1.01683	1.36205
28.4	1.74247	1.31028	1.01733	1.36545
25.85	1.74572	1.31242	1.01765	1.36918
23.4	1.74918	1.31452	1.01806	1.37288
21.08	1.75291	1.31668	1.01842	1.37664
18.89	1.75689	1.31884	1.01877	1.38028
16.75	1.76102	1.321	1.01907	1.38412
14.68	1.76529	1.3232	1.01936	1.38799
12.72	1.76989	1.32531	1.01954	1.39191
10.83	1.77476	1.32756	1.0198	1.3957
9.01	1.77993	1.32969	1.02009	1.39966
7.28	1.78519	1.33179	1.0203	1.40387
5.62	1.79072	1.33403	1.02051	1.40785
4.04	1.79654	1.33609	1.02068	1.41193
2.53	1.80257	1.33831	1.02082	1.41625
1.07	1.8088	1.34037	1.02106	1.42024
-0.3	1.8152	1.34243	1.02123	1.42492
-1.63	1.82215	1.34447	1.02138	1.42907
-2.88	1.82923	1.34666	1.02148	1.43289
-4.08	1.8365	1.34854	1.02163	1.43729
-5.19	1.84411	1.35057	1.02177	1.44107
-6.26	1.85194	1.3524	1.02195	1.44525
-7.27	1.86002	1.35426	1.02202	1.44971
-8.22	1.86864	1.35605	1.02223	1.45358
-9.12	1.87756	1.35785	1.02227	1.45778
-9.94	1.88667	1.35966	1.02239	1.46164
-10.71	1.896	1.36126	1.02247	1.46571
-11.45	1.90573	1.36282	1.02261	1.46986
-12.11	1.91591	1.3643	1.02275	1.47389
-12.72	1.92647	1.36561	1.02282	1.47774
-13.28	1.93706	1.36701	1.02294	1.48174
-13.8	1.94816	1.36823	1.02302	1.48531
-14.26	1.95973	1.36925	1.02311	1.48869
-13.01	1.99858	1.3576	1.0252	1.48736
-9.98	2.054	1.33753	1.02706	1.47876
-10.29	2.06732	1.33796	1.02709	1.4814
-10.59	2.08068	1.33831	1.02705	1.48395

Table 2. $Ni_3(HITP)_2$ bond lengths at different hydrostatic pressure.

Pressure (kB)	Bond Length (Å)				
	Ni-N	N-C	C-H	N-H	C-C
30.73	1.71414	1.2967	1.08209	1.0166	1.33
28.47	1.71614	1.29885	1.08285	1.017	1.33332
26.33	1.71838	1.30086	1.08359	1.01733	1.33641
24.27	1.721	1.30304	1.08433	1.01768	1.33955
22.29	1.72387	1.30527	1.08507	1.01806	1.34275
20.39	1.72712	1.30757	1.08575	1.01841	1.34596
18.55	1.7307	1.30992	1.08641	1.01877	1.34916
16.8	1.73446	1.31224	1.08694	1.01906	1.35253
15.13	1.73873	1.31464	1.08759	1.0194	1.356
13.53	1.74303	1.31702	1.08821	1.01969	1.35929
11.98	1.74797	1.31935	1.08879	1.02	1.36263
10.52	1.75301	1.32163	1.08931	1.02026	1.36603
9.11	1.75823	1.32423	1.08985	1.02048	1.36936
7.74	1.76396	1.32657	1.09041	1.02071	1.37302
6.45	1.76998	1.32898	1.09092	1.02095	1.37638
5.21	1.77613	1.33144	1.09147	1.02116	1.37994
4.02	1.78288	1.33389	1.09187	1.02135	1.38365
2.89	1.78965	1.33633	1.0923	1.02152	1.38729
1.81	1.79683	1.33886	1.09274	1.02172	1.3908
0.78	1.80438	1.34124	1.09312	1.02192	1.39428
-0.2	1.81235	1.34363	1.09355	1.02213	1.39778
-1.13	1.82064	1.34604	1.09391	1.02227	1.40136
-2.01	1.82908	1.34828	1.09424	1.02235	1.40462
-2.84	1.83836	1.35068	1.09455	1.02253	1.40829
-3.64	1.84773	1.35303	1.09489	1.02264	1.41189
-4.38	1.85722	1.35512	1.09516	1.02278	1.41569
-5.1	1.86764	1.35739	1.0954	1.0229	1.41907
-5.76	1.87887	1.35948	1.09574	1.02309	1.42244
-6.37	1.88986	1.36141	1.09591	1.02316	1.42604
-6.93	1.90123	1.36335	1.09613	1.02332	1.42959
-7.47	1.91383	1.3652	1.09638	1.02339	1.43318
-7.97	1.92652	1.36685	1.09653	1.0235	1.4362
-8.42	1.94051	1.36839	1.09668	1.02362	1.43947
-8.84	1.95584	1.36995	1.09675	1.02367	1.44247
-9.19	1.9719	1.37126	1.09691	1.02378	1.44541
-9.52	1.98803	1.37247	1.09704	1.02389	1.44819
-9.81	2.0055	1.3733	1.09715	1.02398	1.45086
-10.05	2.02341	1.37411	1.09721	1.0241	1.45354
-10.24	2.04361	1.37472	1.09731	1.02415	1.45584
-10.38	2.06541	1.37501	1.09743	1.02427	1.45769

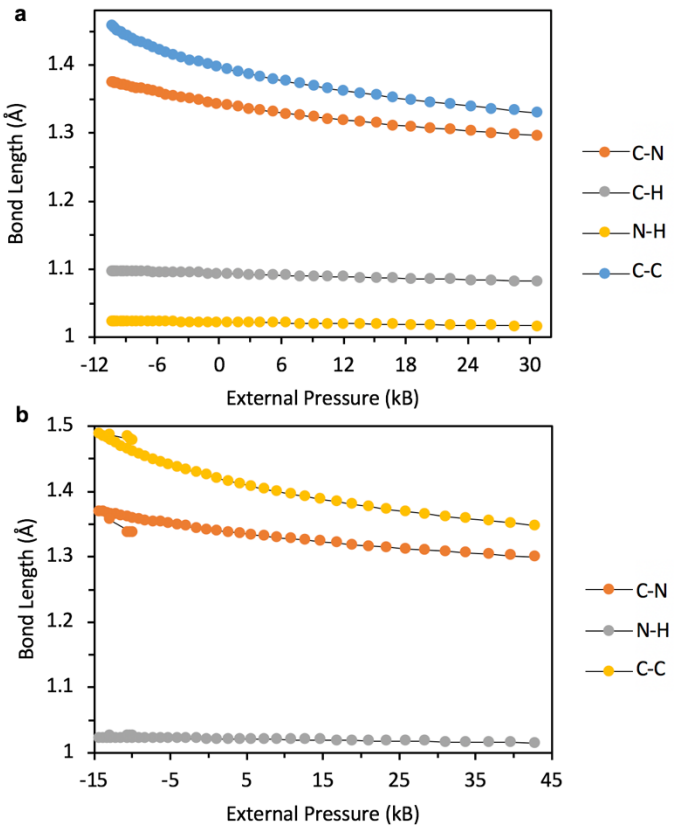

Figure S1. A structural comparison of both (a) $Ni_3(HITP)_2$ and (b) $Ni_3(HIB)_2$ at various external pressure.

Example of unit cell used for the pressure:

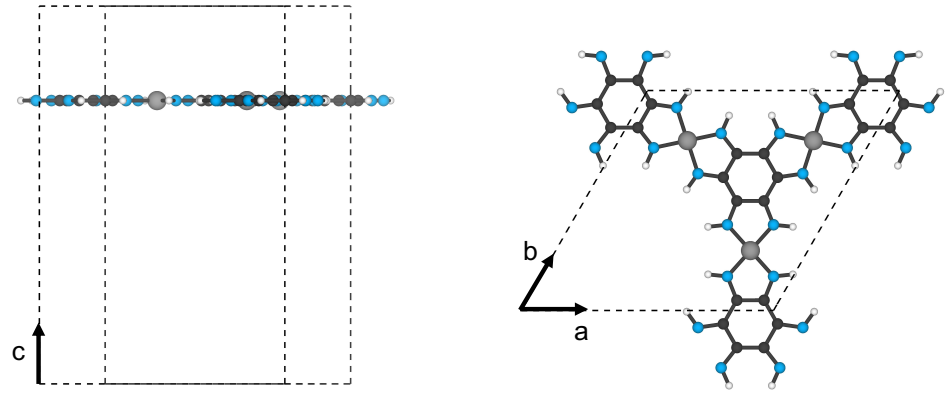

Figure S2. $Ni_3(HIB)_2$ unit cell at lattice constant 1.0. The vacuum lay along the c-direction (left) and the monolayer is parallel to the ab-plane (right).

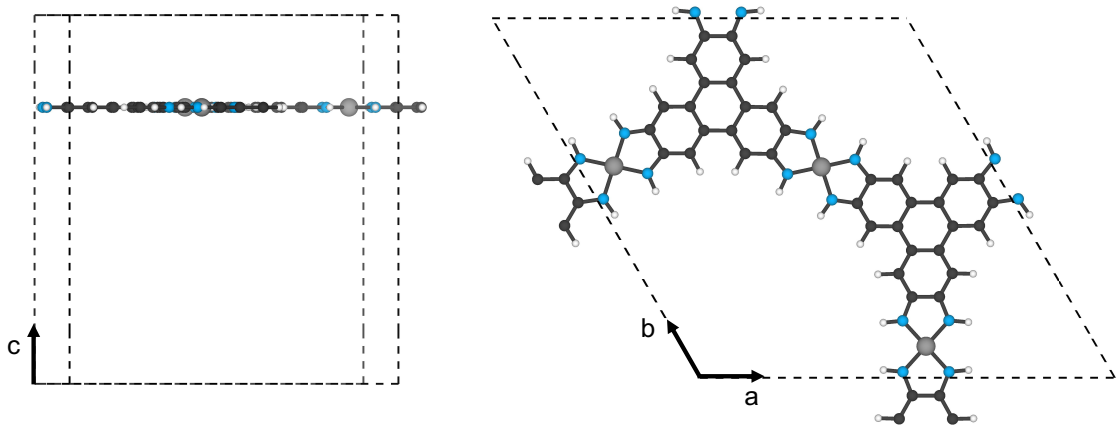

Figure S3. $Ni_3(HITP)_2$ unit cell at lattice constant 1.0. The vacuum lay along the c-direction (left) and the monolayer is parallel to the ab-plane (right).

PBEsol functional compare to GGA functional:

For this study, the most important feature is the closing of the band gap and shift in energy of the Ni-N orbital that cause the change in magnetic properties. For this reason, we chose to use the PBEsol functional for all calculation to minimize computation cost. Hybrid functional such as HSE06 might produce higher quality band structures but very expensive and only contain similar information that can be capture by calculation at the GGA level (Figure 3). As show below, both structure for $Ni_3(HITP)_2$ displace a band gap correspond to a semi-conductive material and no band gap for $Ni_3(HIB)_2$. Both functionals are consistence with one another, hence PBEsol is sufficient for this study.

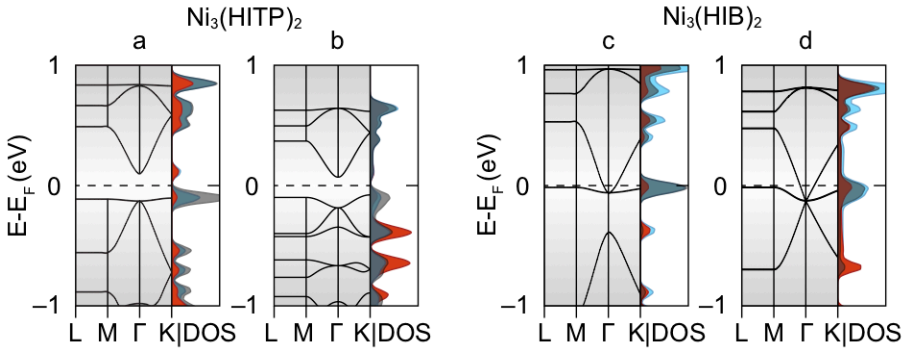

Figure S4. Electronic band structure and density of state of $Ni_3(HITP)_2$ (left) and $Ni_3(HIB)_2$ (right) computed by two different functionals: (a) HSE06 and (b) PBEsol for $Ni_3(HITP)_2$; (c) HSE06 and (d) PBEsol for $Ni_3(HIB)_2$.

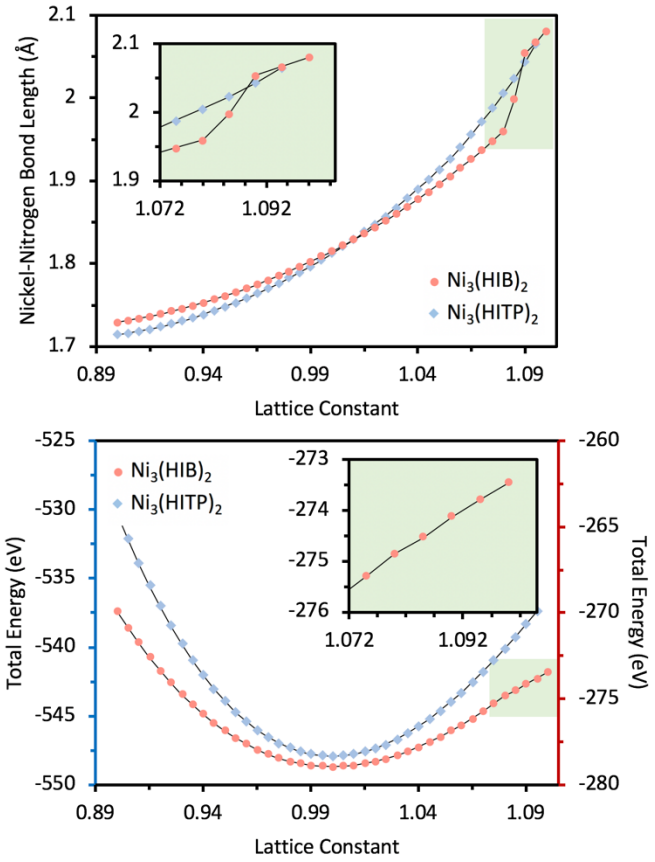

Figure S5. A structural (a) and energetic (b) comparison of both $Ni_3(HITP)_2$ and $Ni_3(HIB)_2$ at various lattice constant. The inset graphs highlight the Ni^{2+} piezoreduction upon expansion of the $Ni_3(HIB)_2$ lattice.