Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Rational Design of an unusual 2D-MOF based on Cu(I) and 4-hydroxypyrimidine-5-carbonitrile as Linker with Conductive Capabilities

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1. **Synthesis of [Cu(4hypymca)]$_n$ (1).** 0.09 mmol (10.00 mg) of 4-Hidroxypyrimidine-5-carbonitrile were dissolved in 0.5 mL of DMF afterwards 0.5 mL of distilled water was added. In another glass vessel 0.06 mmol (15.59 mg) of $CuCl_2 \cdot 2H_2O$ was dissolved in 0.5 mL of distilled water and then 0.5 mL of DMF. The ligand solution were mixed in a closed glass vessel and introduced in an oven at 100 °C for 24 h. yellow single crystals were grown during the heating procedure. The final product was washed with destilled water, and dried in open atmosphere. Yield: 71% based on metal. Anal Calcd for $CuC_5H_2N_3O$: C, 32.70; H, 1.10; N, 22.88. Found: C, 32.65; H, 1.06; N, 22.94.

Elemental analyses (C, H, N) were performed on an Euro EA Elemental Analyzer. FTIR spectra (KBr pellets) were recorded on a Nicolet IR 6700 spectrometer in the 4000–400 cm^{-1} spectral region.

2. X-ray Diffraction. X-ray data collection of suitable single crystal of compound **1** was done at 100(2) K on a Bruker VENTURE area detector equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) by applying the ω-scan method. The data reduction were performed with the APEX2 software[1] and corrected for absorption using SADABS.[2] Crystal structures were solved by direct methods using the SIR97 program[3] and refined by full-matrix least-squares on F^2 including all reflections using anisotropic displacement parameters by means of the WINGX crystallographic package.[4] All hydrogen atoms were included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 times or 1.5 times those of their parent atoms for the organic ligands. Details of the structure determination and refinement of compounds are summarized in Table 1. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 1942013-14 for compounds. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44-1223-335033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table S1. Crystallographic data and structure refinement details for all compounds.

Compound	**1**	**0.9 GPa**	**2.75 GPa**	**2 (4.2 GPa)**
Chemical formula	$C_5H_2N_3OCu$	$C_5H_2N_3OCu$	$C_5H_2N_3OCu$	$C_5H_2N_3OCu$
CCDC	1942013			
M/g mol^{-1}	183.64	183.64	183.64	183.64
T/K	100 K	293 K	293 K	293 K
Cryst. syst.	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pbcm*	*Pbcm*	*Pbcm*	*Pbcm*
a (Å)	8.056 (3)	8.0286(8)	7.9702(8)	7.9478 (16)
b(Å)	10.787 (3)	10.776(10)	10.714(9)	10.61 (2)
c(Å)	6.0093 (18)	5.8800(5)	5.6247(4)	5.5058 (12)
V/ Å^3	522.2 (3)	508.7(5)	480.3(4)	464.3 (9)
Z	4	4	4	4
ρ/g cm^{-3}	2.336	2.398	2.539	2.627
μ/mm^{-1}	4.082	4.191	4.439	4.592
$R[1>2\sigma(I)]^a$	0.0303	0.0645	0.0672	0.0443
$wR^2\ [1>2\sigma(I)]^b$	0.0618	0.2066	0.2069	0.1222

[a] $S = [\Sigma w(F_0^2 - F_c^2)^2 / (N_{obs} - N_{para}m)]^{1/2}$ [b] $R_1 = \Sigma||F_0|-|F_c|| / \Sigma|F_0|$ [c] $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma wF_0^2]^{1/2}$
$w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (\max(F_0^2,0) + 2F_c^2)/3$

3. High-Pressure X-Ray Diffraction

High pressure single crystal study was undertaken using a custom made Diamond Anvil Cell equipped with 0.5 mm culets and a ~40° opening. A small crystal of the sample was loaded in the pre-pressed and drilled steel gasket along with a methanol-ethanol mixture (4:1) and a small ruby sphere for pressure calibration. Data were collected using a single phi scan in the Material Science beamline at the Swiss Light Source, using a focused beam defined by a 150 µm pinhole of 0.49276 Å, as calibrated on the high resolution powder diffractometer using the NIST SRM640d standard. Data were collected using a Pilatus 6M detector calibrated with a NIST ruby sphere (SRM1990) and integrated using the Crysalis package and its high pressure dedicated abilities. Diamond overlapping peaks were masked out of the integration. Despite attempts no lower or higher symmetry were identified for the given datasets up to 4.2 GPa.

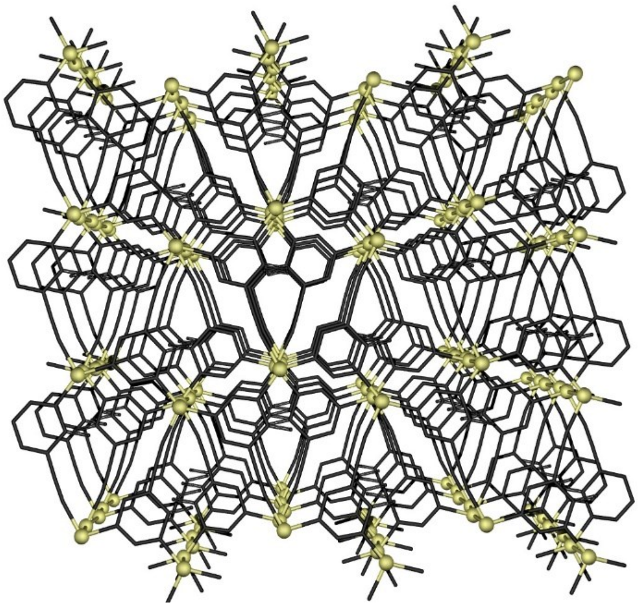
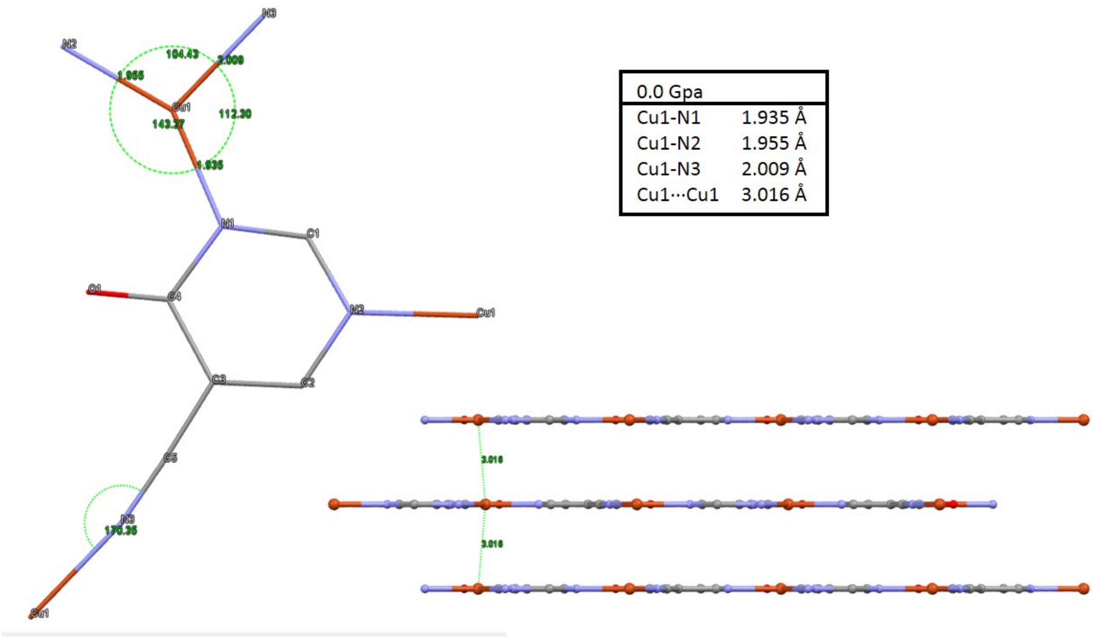
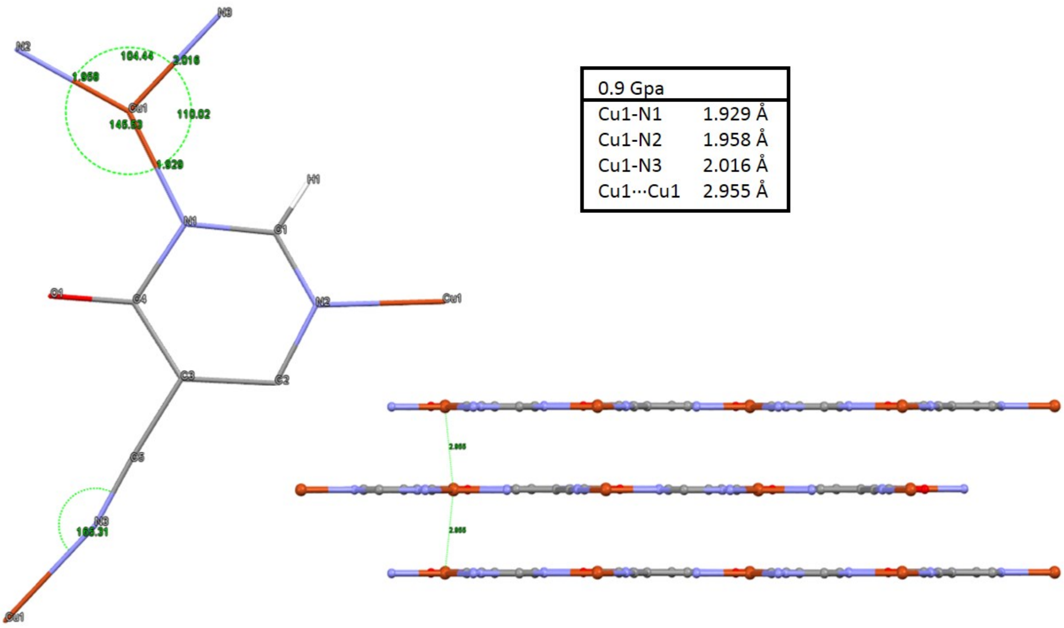


Figure S1. Three-dimensional network formed by C···Cu metal interactions in **1**.



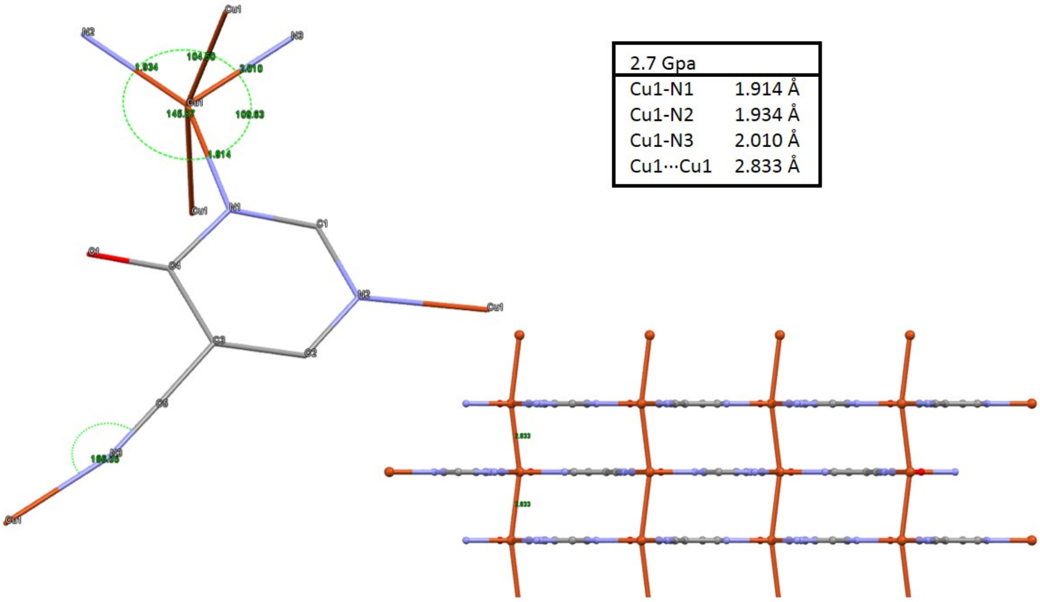
0.0 Gpa	
Cu1-N1	1.935 Å
Cu1-N2	1.955 Å
Cu1-N3	2.009 Å
Cu1···Cu1	3.016 Å

Figure S2. Different perspectives of compound under pressure of 0.0 GPa.



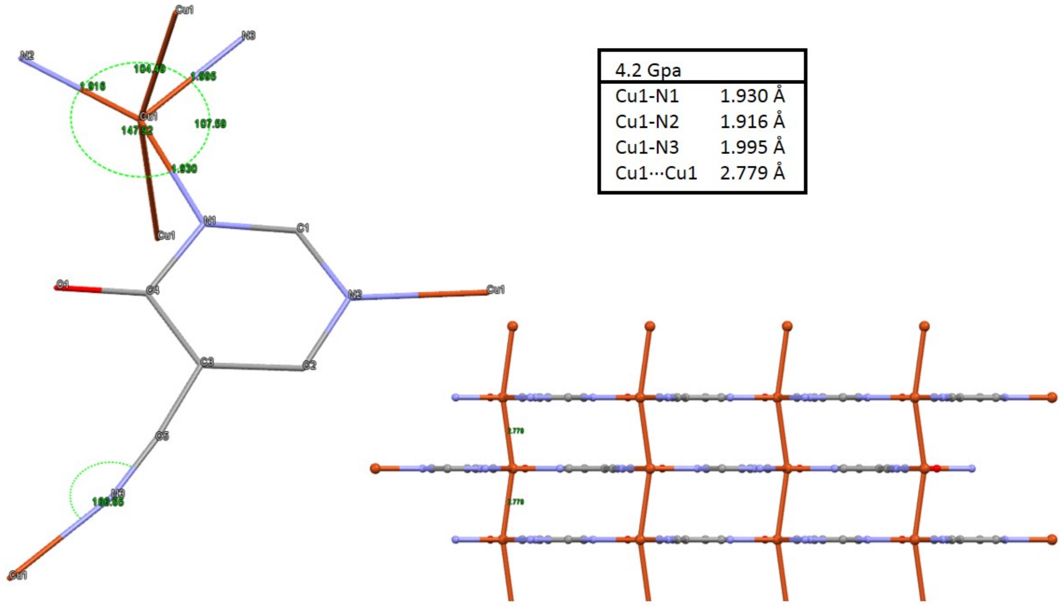
0.9 Gpa	
Cu1-N1	1.929 Å
Cu1-N2	1.958 Å
Cu1-N3	2.016 Å
Cu1···Cu1	2.955 Å

Figure S3. Different perspectives of compound under pressure of 0.9 GPa.



2.7 Gpa	
Cu1-N1	1.914 Å
Cu1-N2	1.934 Å
Cu1-N3	2.010 Å
Cu1···Cu1	2.833 Å

Figure S4. Different perspectives of compound under pressure of 2.7 GPa.



4.2 Gpa	
Cu1-N1	1.930 Å
Cu1-N2	1.916 Å
Cu1-N3	1.995 Å
Cu1···Cu1	2.779 Å

Figure S5. Different perspectives of compound under pressure of 4.2 GPa.

4. Additional information on the computational results.

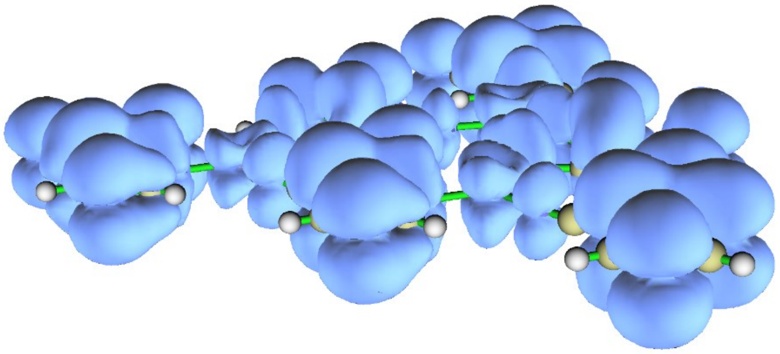
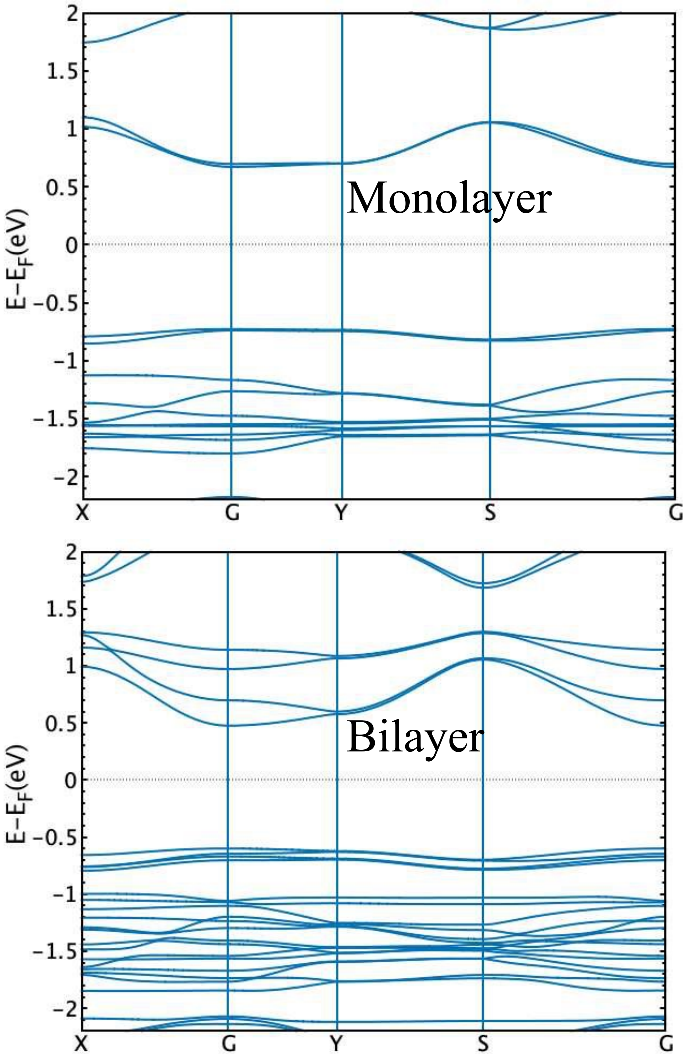


Figure S6. Electron localization function (ELF) representation for the electronic π system on a $Cu_3L_6^{3-}$ fragment.



FigureS7. Band structure for an isolated single layer (upper panel) and for two consecutive layers (lower panel).

Table S2: Bond lengths (Å) and angles (deg) in the original and compressed materials.

	Original compound	**0.9 GPa**	**2.7 GPa**	**4.2 GPa**
Cu-N1	1.935(5)	1.93(3)	1.92(2)	1.93(3)
Cu-N2	1.955(5)	1.96(4)	1.94(3)	1.91(3)
Cu-N3	2.009(6)	2.01(2)	2.012(19)	1.996(19)
Cu1···Cu1	3.0160(9)	2.9549(11)	2.8333(10)	2.7786(13)
N1-Cu-N2	143.3(2)	145.6(13)	145.9(10)	147.9(11)
N1-Cu-N3	112.3(2)	110.0(17)	109.5(14)	107.6(14)
N2-Cu-N3	104.4(2)	104.4(12)	104.6(9)	104.5(9)
Cu1-N3-C5	170.4(5)	166(3)	166(3)	166(3)
Cu1···Cu1···Cu1	170.04(5)	168.5(4)	166.1(3)	164.4(4)

In general, replacing oxygen with any atom having a lower number of valence electrons would generate an excess of electrons and bring the chemical potential closer to the conduction band. Obviously, the lower the valence the closer the chemical potential will get to this band. Below we show two examples (which have now been included in the Supporting Information): energy band structure obtained by replacing 1:4 O with 1 C atom (Figure S5) and with 1 Li atom (Figure S6). Employing C, which has only two electrons less than O, affects the shape of the conduction band but it does not locate the chemical potential close enough to it. Conversely, using Li, which has the same valence as H, results into a similar shift as that observed for H.

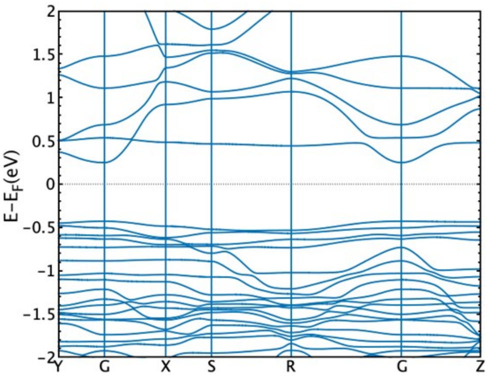


Figure S8: Band structure obtained by replacing 1:4 O atom with a C atom.

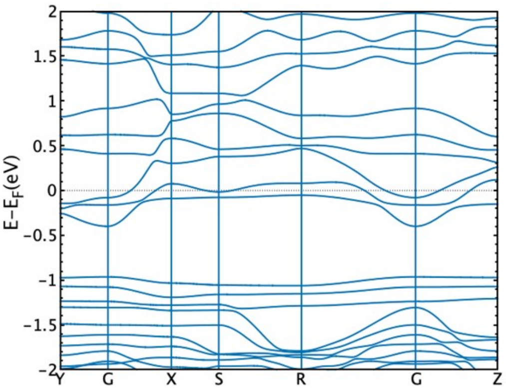


Figure S9: Band structure obtained by replacing 1:4 O atom with a Li atom.

In Figure S6, we show a comparison between the density of states for the original and the compressed material. It can be observed that the upper edge of the valence band is closer to the Fermi level in the compressed material than in the original compound. This is consistent with the narrowing of the gap we observed in the band structure at the G point (Figure 4 of the main text).

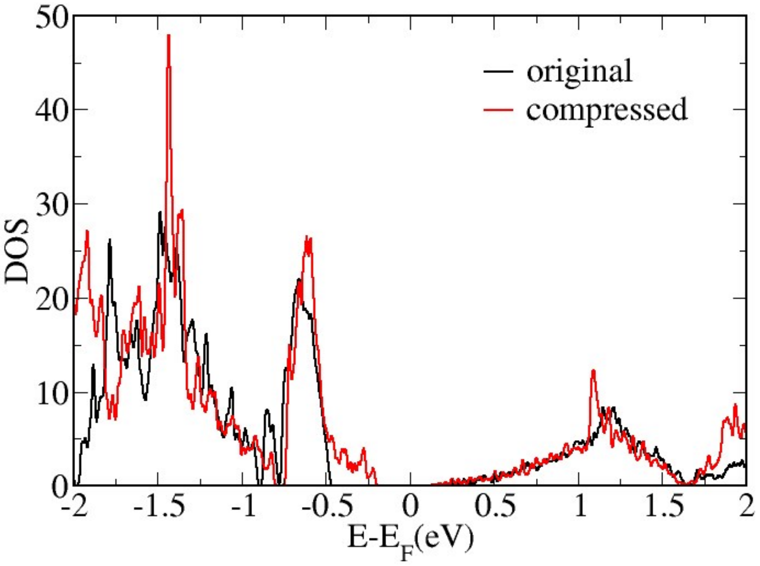


Figure S10: Total density of states (DOS) for the original (black) and compressed (red) material.

The following figure shows that the aforementioned gap narrowing is also visible in the comparison between the projected density of states (PDOS) on the Cu ion in the two materials. The higher values obtained in the energy region below the Fermi level can be ascribed to the overall flatness of the valence-band structure; conversely, the lower values in the energy region above it probably originate from the much-more pronounced curvature of the conduction band.

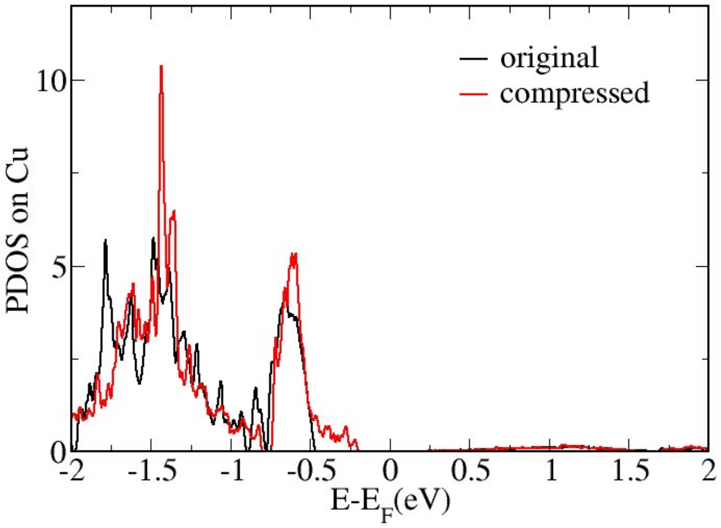


Figure S11: Projected density of states on the Cu ion in the original (black) and compressed (red) material.

Notes and references

1 Bruker Apex2, Bruker AXS Inc., Madison, Wisconsin, USA, 2004.

2 Sheldrick, G.M. SADABS, Program for Empirical Adsorption Correction, Institute for Inorganic Chemistry, University of Gottingen, Germany, 1996.

3 Altomare, A.; Burla, M. C.; Camilla, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A. Moliterni A. G. G.; Polidori, G.; Spagna, *J. Appl. Cryst*., 1999, **32**, 115-119.

4 (a) Sheldrick, G. M. SHELX-2014, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 2014. (b) Farrugia, *J. Appl. Cryst*., 1999, **32**, 837-838.