

Supporting Information

An unusual triple parallel interpenetrated 2D Cu-polymer, with a 3D triple interpenetration via H-bonding

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Experimental Section

Materials. All chemicals were of reagent grade and were used as commercially obtained. FTIR spectra (KBr pellets) were recorded on a Perkin-Elmer 1650 spectrophotometer. Elemental analyses were performed on a Perkin-Elmer 240-B microanalyzer.

Synthesis and Characterization of $[\text{Cu}_2(\text{CN})(\text{IN})(\text{HIN})]_n$ (1): A mixture of CuCN (0.800 g, 8.94 mmol), isonicotinic acid (HIN) (2.200 g, 17.86 mmol) and H_2O (8 mL) was stirred at room temperature and the pH adjusted to 2.2 with HNO_3 (0.1 mol/L). Then, the mixture was sealed in a 23 mL teflon-lined autoclave and heated at 180 °C for 4 days. Afterwards, the autoclave was slowly cooled up to 20 °C. The resulting yellow crystals were filtered off, washed with water and dried in air. (0.500 g, 28.1 % yield). *Anal.* Calcd (found) for $\text{C}_{13}\text{H}_9\text{Cu}_2\text{N}_3\text{O}_4$: C, 39.17 (37.85); H, 2.26 (2.18); N, 10.54 (10.77). IR (KBr, cm^{-1}): 3431s; 2150m; 1720m; 1614s; 1606s; 1412s; 1384s; 1230s; 1053w; 881w; 765m; 746m, 683m.

X-ray Data Collection and Structure Determination. Data collections on single crystals of compound **1** were carried out with an Xcalibur diffractometer equipped with an area detector and graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). The data reduction was done with the CrysAlis RED program [S1]. Data were corrected for Lorentz and polarization effects. The structures were solved by direct methods using the SIR 97 program [S2]. Full matrix least squares refinements were performed on F^2 using SHELXL97 [S3]. All non-hydrogen atoms were refined anisotropically. The cyanide bridge was modeled as disordered with C/N composites, occupancy 0.5 each. The hydrogen atoms belonging to the aromatic rings were placed in geometrically calculated positions and treated as riding on their parents atoms [C-H: 0.93 Å and

$U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$. The hydrogen atom of the carboxylic group was located in the Fourier difference map and isotropically refined. All calculations were performed using the WinGX crystallographic software package [S4]. The final geometrical calculations and the graphical manipulations were carried out with the PARST95 [S5] and PLATON [S6] programs. Summaries of crystal data collection and refinement parameters are given in Table S1.

References

- [S1] *CrysAlis RED*, version 1.170; Oxford Diffraction: Wroclaw, Poland, 2003.
- [S2] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, 32, 115-119.
- [S3] G. M. Sheldrick, *SHELXL97*; University of Göttingen:, Germany, 1997.
- [S4] L. J. Farrugia, *WINGX. A Windows program for crystal structure analysis*; University of Glasgow, U.K., 1998.
- [S5] M. J. Nardelli, *Appl. Crystallogr.*, 1995, 28, 659-673.
- [S6] A. L. Spek, *PLATON, A multipurpose crystallographic tool*; Utrecht University, The Netherlands, 1998.

Table S1. Crystal data, data collection, and structure refinement for compound **1**.

empirical formula	C ₁₃ H ₉ Cu ₂ N ₃ O ₄
formula weight	398.32
crystal system	monoclinic
space group	Pc
<i>a</i> (Å)	10.864(2)
<i>b</i> (Å)	5.116(1)
<i>c</i> (Å)	12.282(2)
β (°)	104.53(1)
<i>V</i> (Å ³)	660.8(2)
<i>Z</i>	2
F(000)	396
D _{calc} (g cm ⁻³)	2.002
μ (mm ⁻¹)	3.240
T (K)	293(2)
Max θ (°)	30
reflections collected	6073
independent reflections	3232
reflections observed [$I \geq 2\sigma(I)$]	2367
data/restraints/parameters	3232, 0, 204
flack parameter	Racemic twin, BASF 0.40(4)
final <i>R</i> indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0298^a$ $wR_2 = 0.0727^b$
<i>R</i> indices (all data)	$R_1 = 0.0438^a$ $wR_2 = 0.0756^b$
goodness-of-fit <i>S</i> on F^2	0.947
largest difference peak and hole (e Å ⁻³)	0.475 and -0.572

^a $R_1 = \Sigma (||F_O| - |F_C||) / \Sigma |F_O|$. ^b $wR_2 = [\Sigma w(|F_O| - |F_C|)^2 / \Sigma w|F_O|^2]^{1/2}$

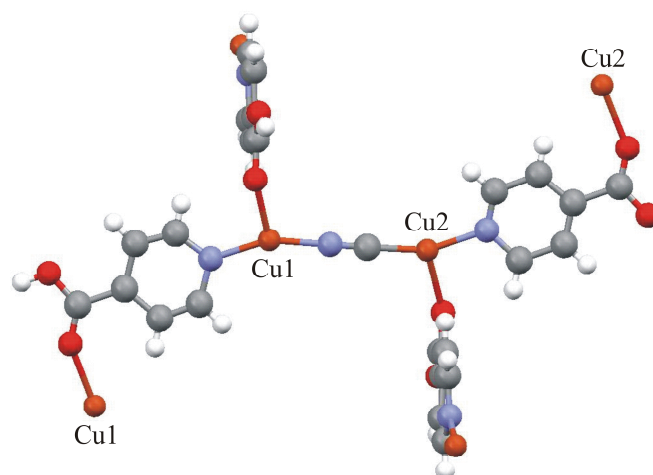


Figure S1. Detailed view of the coordination polymer showing the two different coordination environments of the Cu atoms (Cu orange; O red; N blue, C grey, H white).

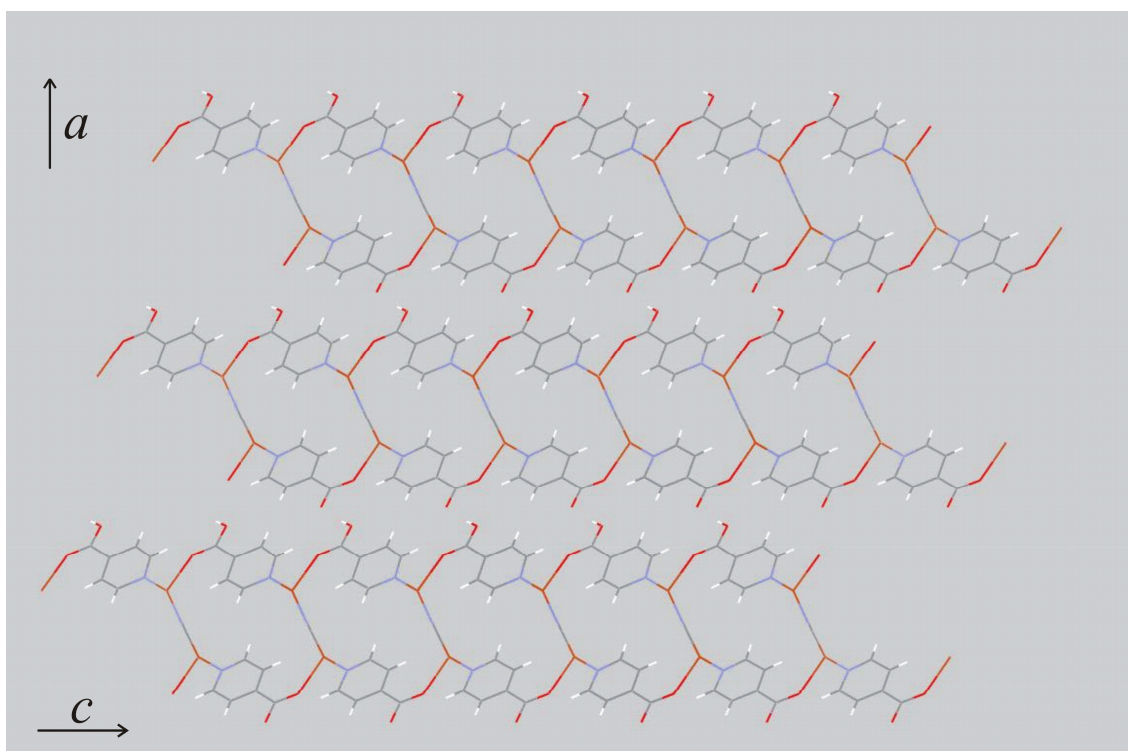


Figure S2. View of the hydrogen-bonding between the 2D-threefold interpenetrated networks.

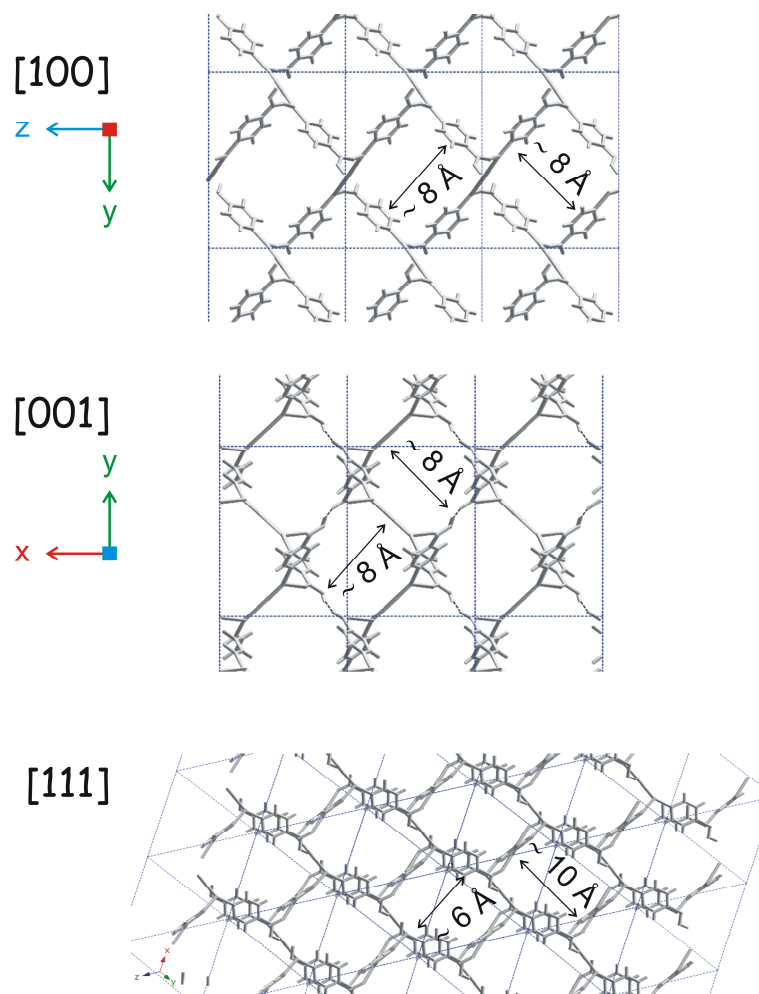


Figure S3. Theoretical open framework in the absence of interpenetration.

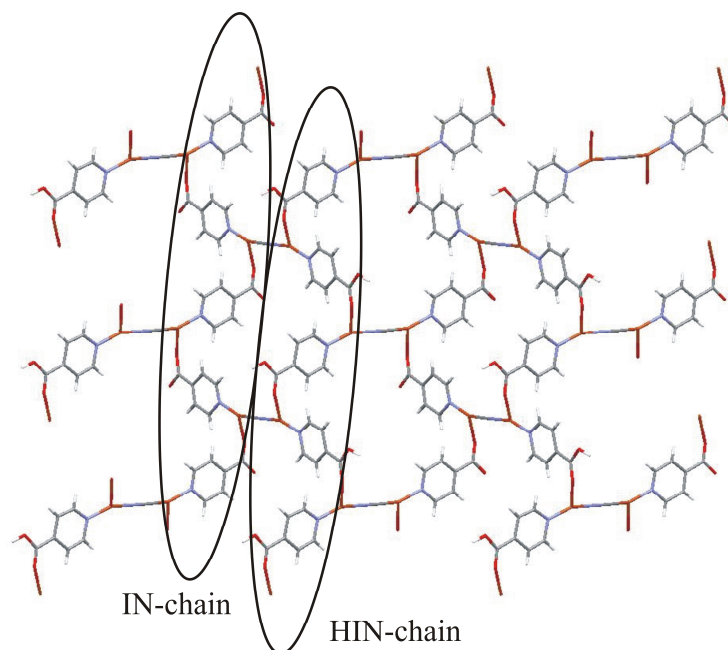


Figure S4. Disposition of the HIN (Cu1) and IN (Cu2) chains.

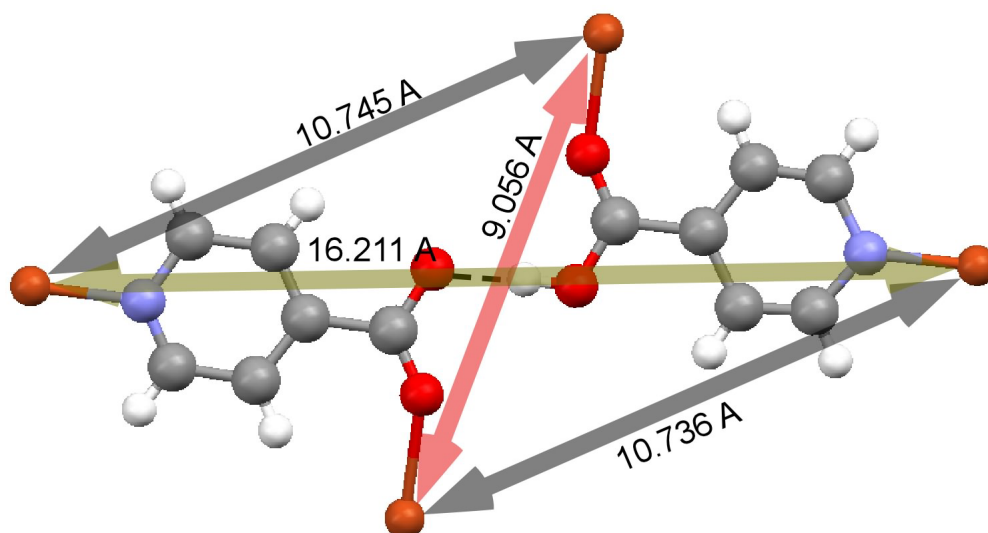


Figure S5. Possible connections of the nodes through the hydrogen bonding interaction.

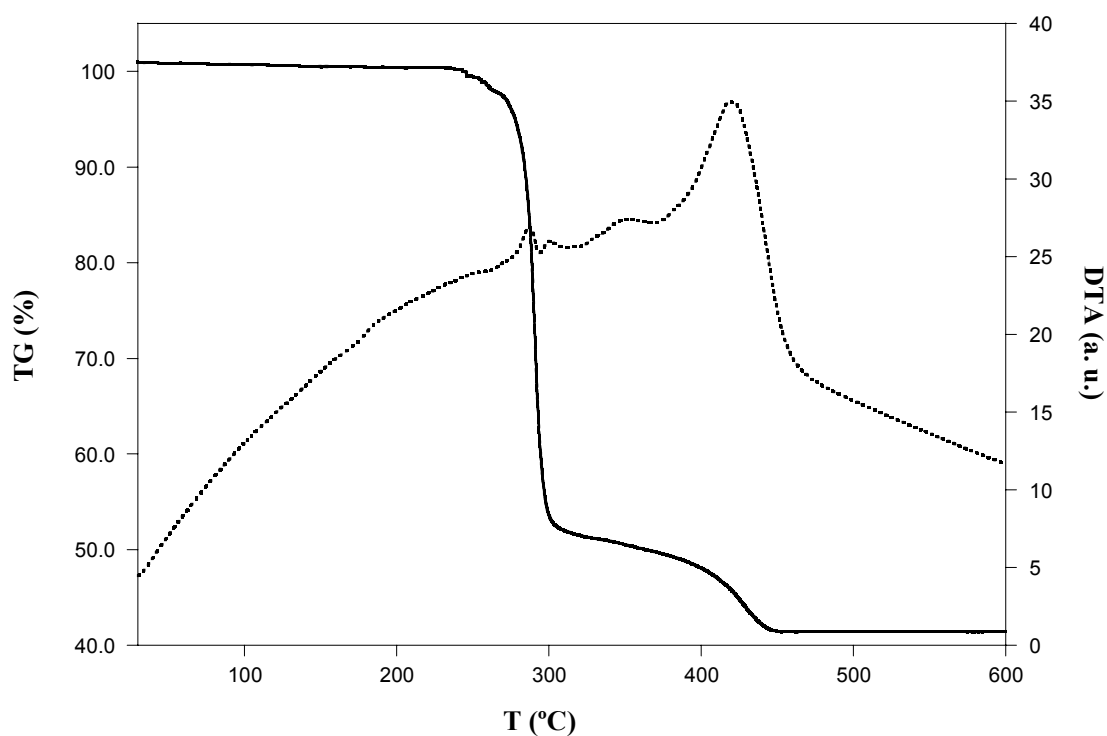


Figure S6. Thermal analysis (TG/DTA) were performed on a TA Instruments SDT 2960 thermal analyzer in a synthetic air atmosphere (79 % N₂ / 21 % O₂) with heating rate of 5 °C min⁻¹ from room temperature to 600 °C. Residue: Exp. 40.31 %, Calc.(CuO) 39.92 %.