Single layers of a multifunctional laminar Cu(I,II) coordination polymer

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Supporting Information

Experimental Procedure

Materials and Methods

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 by the Microanalysis Service of the University Autónoma of Madrid on a Perkin-Elemer 240 B microanalyzer.

Variable–temperature magnetic susceptibilities were measured on polycrystalline samples with a Quantum Design MPMS-XL SQUID susceptometer in the temperature range 2-300 K with an applied magnetic field of 1 Tesla. All the data were corrected for the diamagnetic contribution of both the sample holder and the compound. The diamagnetic contributions of the complexes were calculated with the Pascal's constants tables.

Luminescence excitation and emission spectra of the solid compounds were recorded by a JASCO FP-6500 spectrofluorometer using a diode laser with emission at 355 nm (50 mW) and a sample holder developed for powders at 298 K.

Synthesis of $[Cu_2Br(IN)_2]_n$ (**1**). A mixture of $CuBr_2$ (0.5 g, 2.24 mmol), isonicotinic acid (HIN) (0.27 g, 2.24 mmol), potassium hydroxide (0.12 g, 2.24 mmol) and potassium bromide (0.26 g, 2.24 mmol) in 15 mL of water, was stirred at 20 ºC for 1 h. Then, the mixture was loaded in a 23 mL Teflon-lined autoclave and heated at 160 ºC for three days. The autoclave was allowed to reach room temperature naturally. In the mixture of reaction we got three different types of crystals which were separated by hand under an optical microscope. The green crystals obtained correspond to the known $[Cu(H_2O)_4(IN)_2]$ complex,[1] (0.12 g, yield 14 % based on Cu), the red crystals to the already reported[2] $[CuBr(HIN)]_n$ 1D coordination polymer (0.05 g, yield 5.8 % based on Cu) and the dark-red crystals to compound **1** (0.30 g, 40.5 % yield, based on Cu). Selected data for **1**: Anal. Calc. for $C_{12}H_8N_2O_8BrCu_2$: C 31.94 %, H 1.79 %, N 6.21 %. Found: C 31.81 %, H 1.77 %, N 6.25 %. IR selected data (KBr, cm^{-1}): 3420 m, 2917 w, 1633 s, 1614 s, 1512 m, 1416 s, 1382 s 1228 w, 1204 w, 1051 w,1021 w, 857 m, 770 m, 706 w.

Conductivity Measurements

AC electrical conductivity measurements in the 100-400 K range were carried out on four single crystals of compound **1** with the two contacts method (since the crystals were very small). The contacts were made with Pt wires (25 μm diameter) along the best developed face of the crystals using graphite paste. The samples were measured in a Quantum Design PPMS-9 with A.C. currents of 10 μA and different AC frequencies in the range 1-1000 Hz. The four crystals showed similar conductivity values and thermal behaviors. The cooling and warming rates were 0.5 K/min and the results were, within experimental error, identical in the cooling and warming scans. Given the high resistance of the sample, none of the crystals could be measured at temperatures below 100 K since the resistance overpassed the internal impedance of our measurement equipment (100 GΩ).

Scanning Electron Microscopy

The morphology and microstructure of crystals of **1** were analyzed by Scanning Electron Microscopy (SEM) (JEOL JM6400). The substrates used for SEM copper discs from E.M.S Company. The solid material was directly deposited onto the discs.

Atomic Force Microscopy

Atomic Force Microscopy images were acquired in dynamic mode using a Nanotec Electronica system (www.nanotec.es). Olympus cantilevers were used with a nominal force constant of 0.75 N/m. The images are processes using WSxM (freely downloadable SPM software from www.nanotec.es) operating at room temperature in ambient air conditions.

Preparation of the Substrates. In order to prepare the samples for the AFM characterization of the compound on surface, Highly Oriented Pyrolitic Graphite (HOPG) commercially available (NT-MDT Co) were used as substrates. Before the chemical deposition, the HOPG surfaces were cleaved with adhesive tape.

Sample Preparation. 1 mg of $[Cu_2Br(IN)_2]_n$ were suspended in 1 ml of H_2O and sonicated 30 minutes using a ultrasounds probe (Hielscher UP400S ultrasonic processor/ power= 400 w, frequency 24 khz, amplitude= 50 %). The first 15 minutes the polymer water solution was sonicated using an intermittent pulse and the last 15 minutes a continuous pulse was used for the sample sonication. After the ultrasounds treatment a dispersion of **1** in water was obtained and diluted to a concentration of 10^{-6} mg/mL and 10^{-10} mg/mL. 40 µl of the diluted solutions were deposited on HOPG. Upon standing 5 min. on the HOPG at 20 ºC, the substrates were washed with water and then dried under an argon flow.

X-ray Crystallography

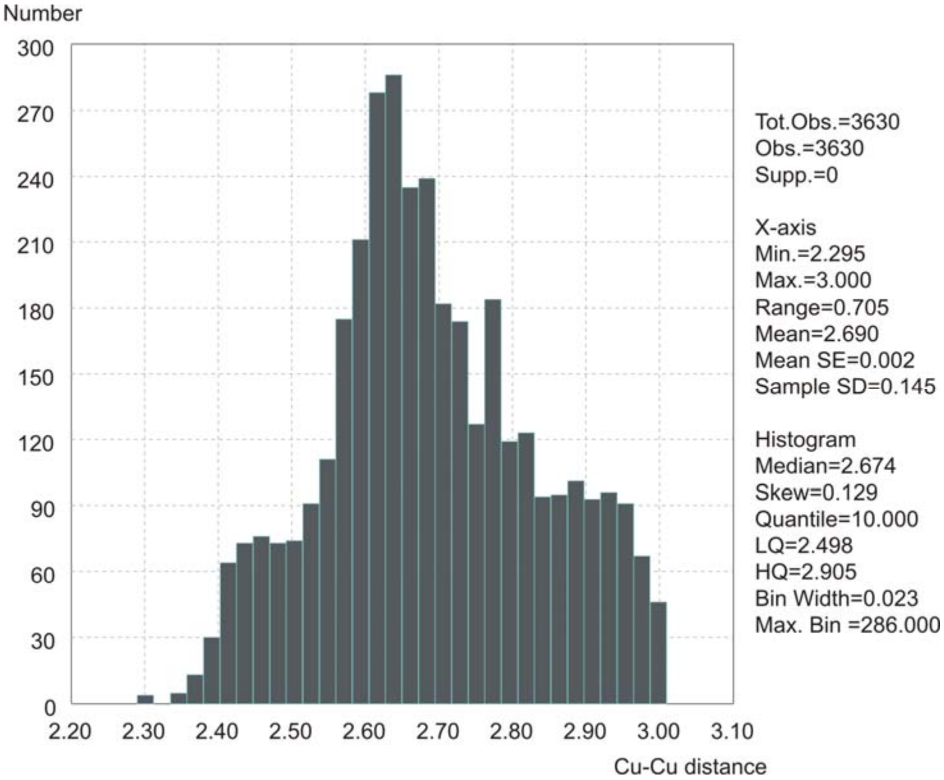
X-ray crystal data for **1** were recorded at 150 K with an Xcalibur diffractometer equipped with an area detector and graphite monochromated Mo Kα radiation (0.71073 Å). Data reduction was done with the CrysAlisPro software.[3] The structure was solved by direct methods and refined by full-matrix least-squares methods based on F^2 using SHELXL-97.[4] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and refined with isotropic displacement parameters according to the riding model. All calculations were performed using the SHELXL-97 and WinGX programs.[4,5]

References

1. N. Okabe, T. Nakamura and H. Fukuda, *Acta Cryst. Sect. C-Cryst. Struct. Commun.*, 1993, **49**, 1761-1762.
2. J. H. Yu, J. Q. Xu, L. Ye, H. Ding, W. J. Jing, T. G. Wang, J. N. Xu, H. B. Jia, Z. C. Mu and G. D. Yang, *Inorg. Chem. Commun.*, 2002, **5**, 572-576.
3. CrysAlisPro, Oxford Diffraction (Poland), 2009.
4. G. M. Sheldrick, SHELXS97 and SHELXL97; University of Göttingen (Germany), 1997.
5. L. J. Farrugia, WinGX; University of Glasgow (Great Britain), 1998.

X-ray additional data for analysis

Graphic representation of the X-ray structures with Cu-Cu distance range: 2 – 3 Å taken from the Cambridge Database (September 16, 2009):



X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) analysis of the sample was carried out in an ultra high vacuum chamber equipped with an hemispherical electron analyser, and using a Al Kα X-ray source (1486.6 eV) with an aperture of 4mm x 7mm. The base pressure in the chamber was 5 x 10^{-10} mbar, and the experiments were performed at room temperature. The following core level peaks were recorded under the same experimental conditions: O(1s), C(1s), N(1s), Cu(2p) and Br(3d). The pass energy applied for taking the overview sample was 30 eV, while 20 eV pass energy was applied for the fine analysis of the core level spectra.

Figures for ESI

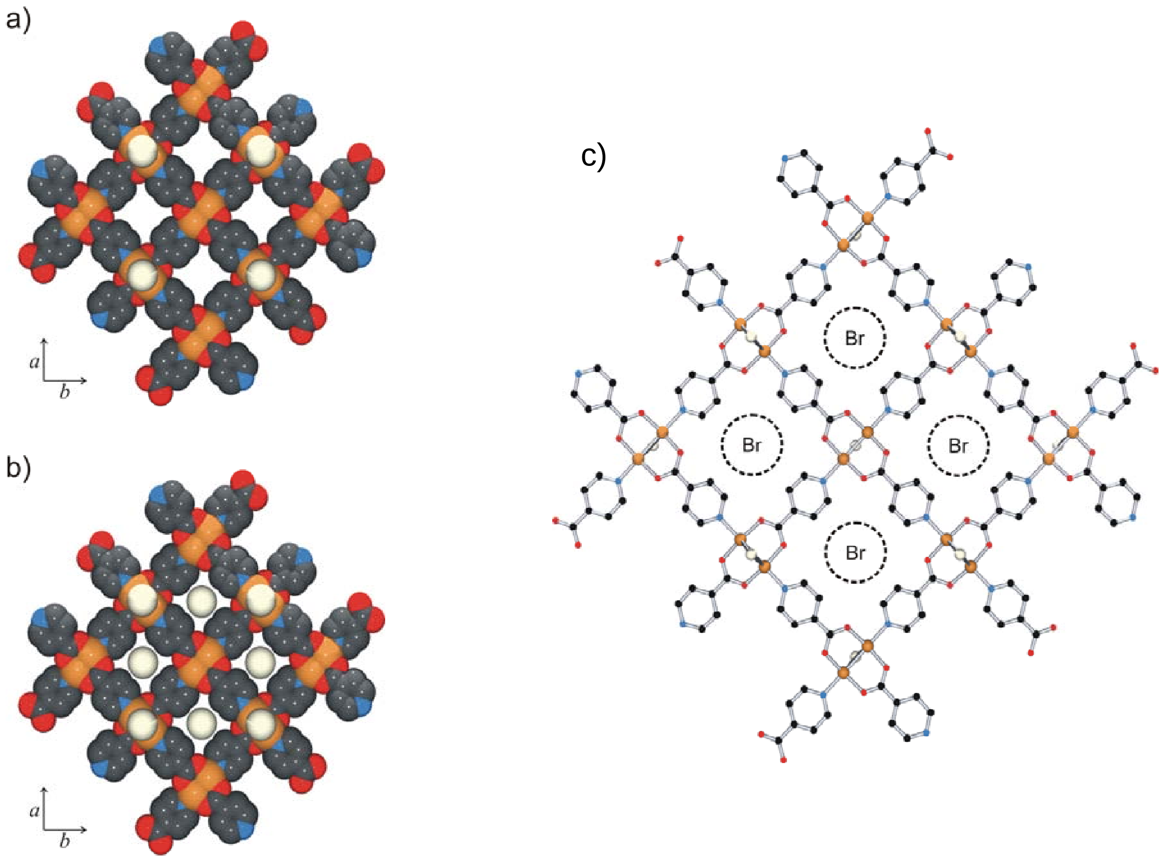


Fig. S1 Space filling representation of a layer fraction of **1** (a). Br ligands from adjacent layers are inserted within the square cavity (b and c).

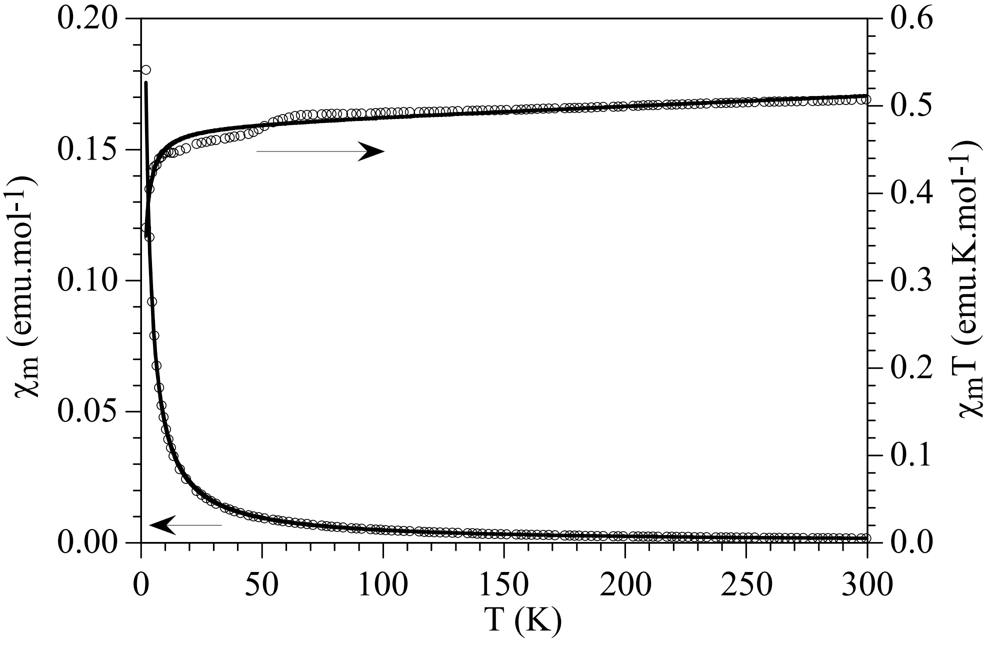


Fig. S2 Thermal variation of the molar magnetic susceptibility (χ_m) per Cu dimer and the χ_mT product for compound **1**. Solid lines represent the best fit to the QLAF model (see main text).

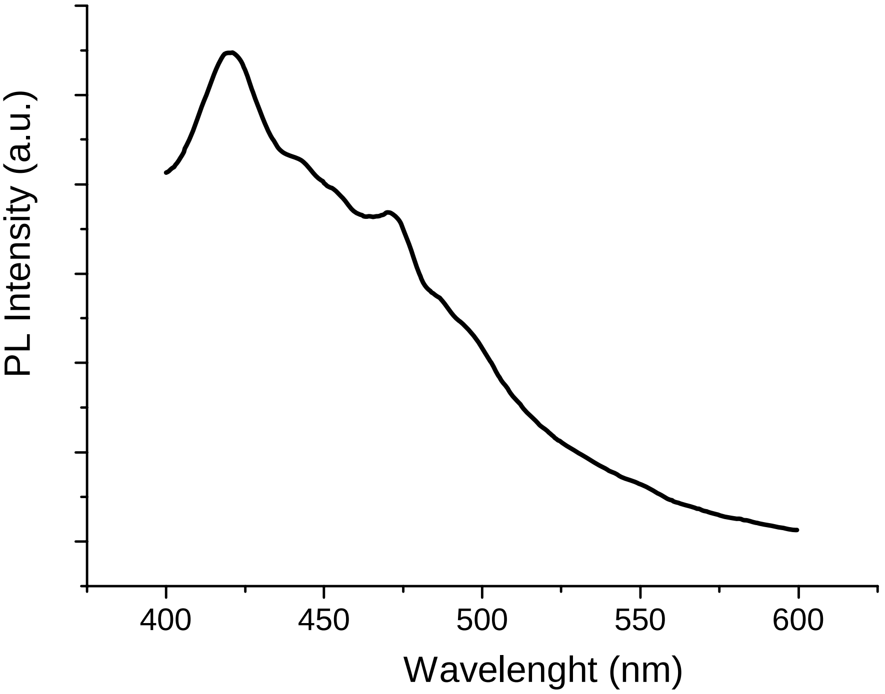


Fig. S3 Emission spectra of **1** in the solid state at λ_{exc} 350 nm.

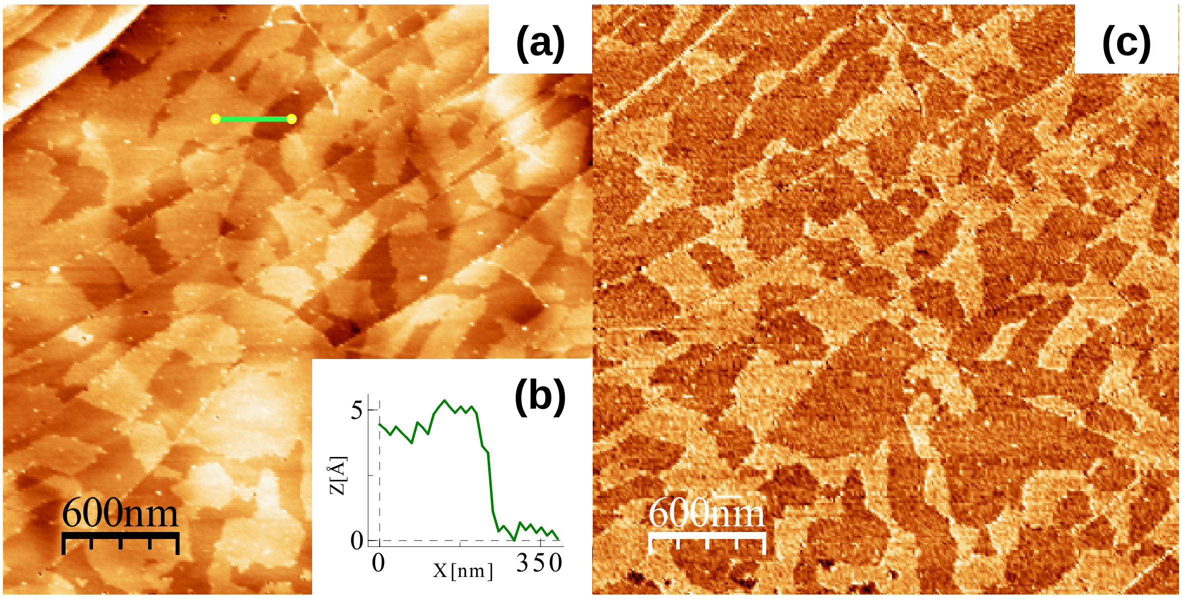
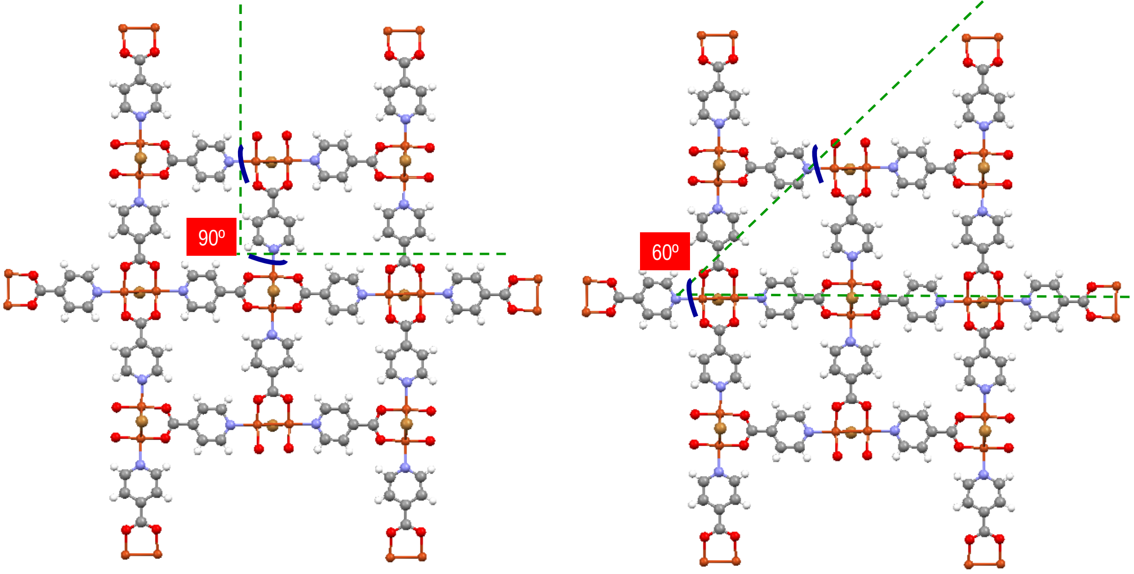


Fig. S4 (a) AFM topography image of a 10^{-10} mg/mL $[Cu_2Br(IN)_2]_n$ solution adsorbed on HOPG. (b) Height profile across the green line in (a). (c) AFM phase image of (a).



(a) (b)

Fig. S5 Representation of the Cu-N coordination bond cleave (solid blue line) between perpendicular (a) and parallel (b) crystallographic axis and the expected geometry (angles) of the resulting layer.

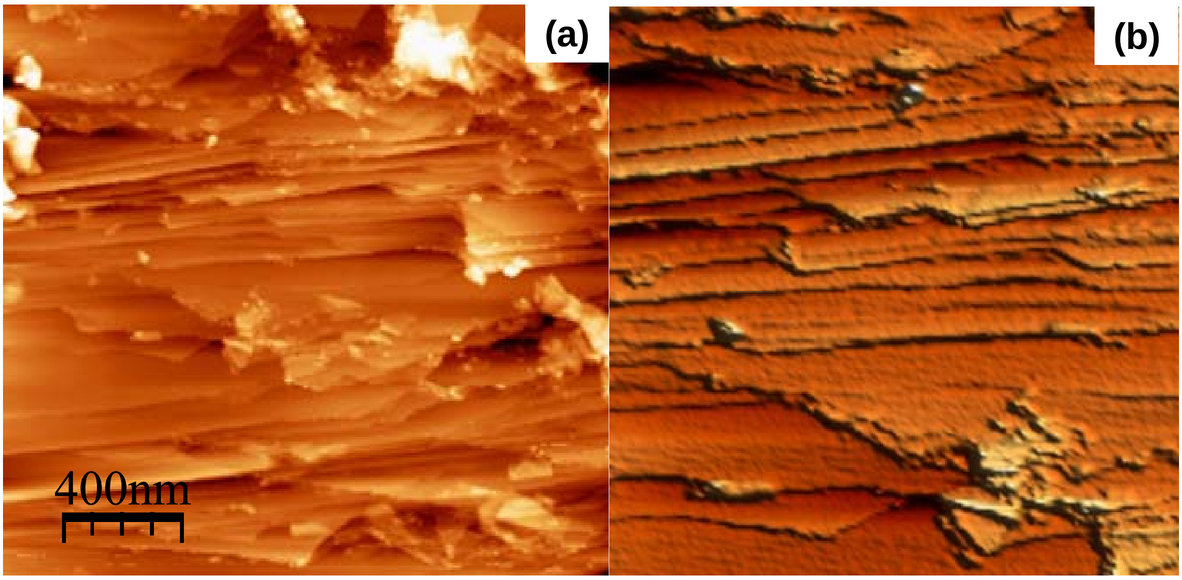


Fig. S6 (a) AFM topography image of a 10^{-6} mg/mL $[Cu_2Br(IN)_2]_n$ solution adsorbed on HOPG. (b) 3D detail of (a) in which is possible to see the layered structure of the compound.

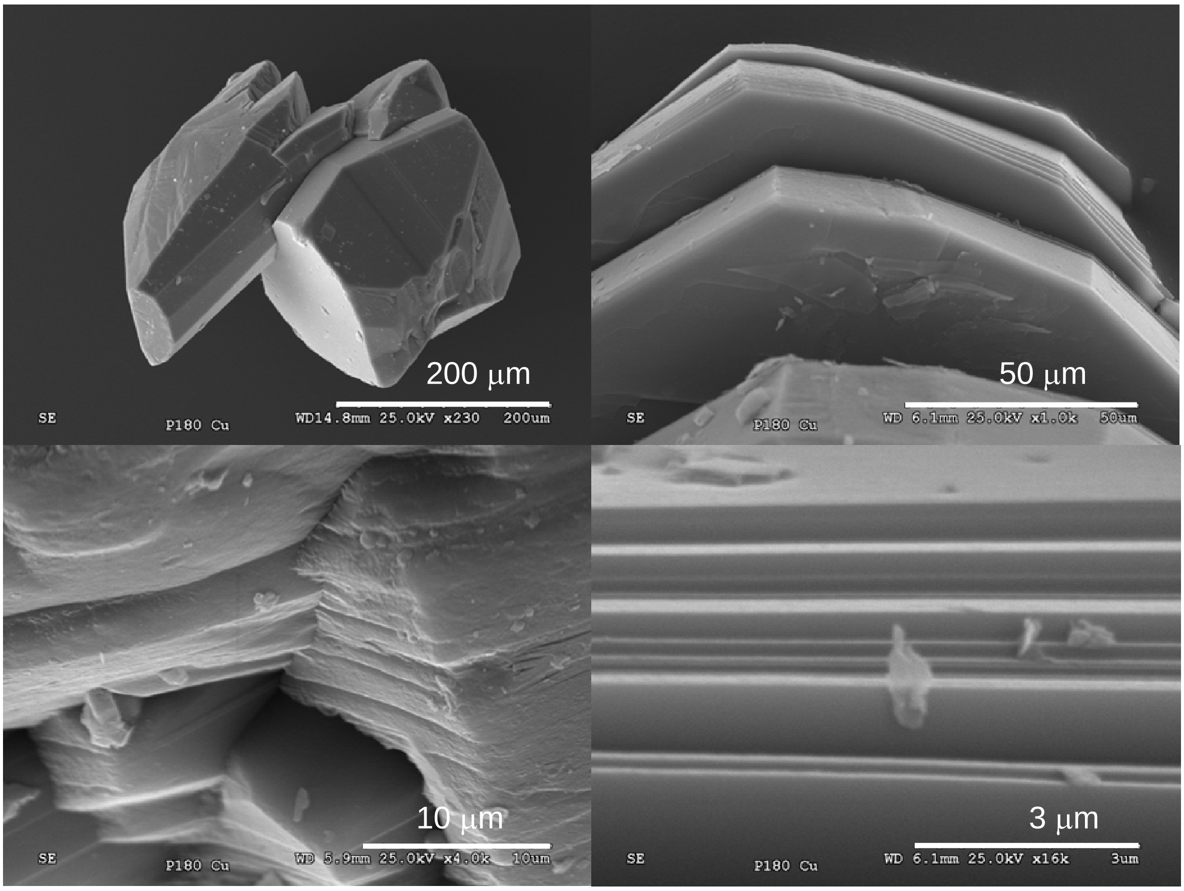


Fig. S7 Selected scanning electron micrographs showing the lamellar structure of **1.**

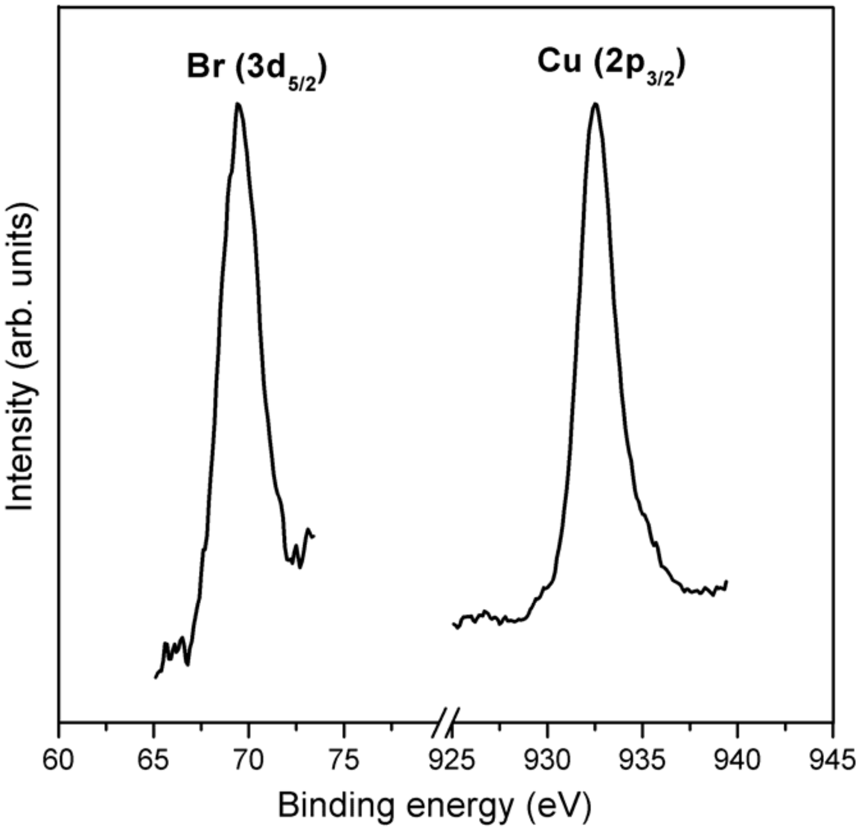


Fig. S8 XPS spectra after adsorption of **1** on HOPG (core-level spectra of the Br (3d$_{5/2}$) and the Cu (2p$_{3/2}$).