Low-Dimensional Polymer

· salve-project.de/newspress/low_d_polymer.html

January 21, 2025 – Researchers from Technische Universität Dresden, Ulm University, the Max Planck Institute of Microstructure Physics, the University of Göttingen (all Germany), the University of Cambridge (UK) and the University of Hong Kong have synthesized a new electrically conductive coordination polymer, Cu_5BHT, with a low-symmetry structure. It conducts like a metal and carries current about eight times better along one crystal direction than along the others. Aberration-corrected electron microscopy at Ulm University resolved the unusual arrangement of its building blocks.

Electrically conductive coordination polymers (ECCPs) and two-dimensional conjugated metal–organic frameworks (c-MOFs) combine metal ions and organic molecules into extended networks. Their electrons are shared within each layer through π–d conjugation, the overlap of the organic π orbitals with the metal d orbitals, and between neighbouring layers through electronic coupling. Depending on the composition, this makes them semiconductors or even metals.[1,2] Because they are assembled bottom-up from molecules, their electronic structure can be tailored at the molecular level, which makes them candidates for next-generation electronic and quantum applications.[3]

The ECCP family has grown rapidly, above all with periodic networks of square, honeycomb and Kagome lattices. These are usually built from square-planar MX_4 linkages, where M is a metal ion and X is O, NH or S, combined with conjugated organic ligands such as benzenehexathiol (BHT),[1,3] hexahydroxybenzene (HHB)[4] and hexaiminotriphenylene (HITP).[5] Nonporous ECCPs built from benzene-derived units, such as Cu_xBHT (x = 3, 4, 5.5),[1,3] Cu_3HHB[4] and Cu_4DHTTB (DHTTB = 2,5-dihydroxy-1,3,4,6-tetrathiolbenzene),[6] are particularly interesting: they adopt a Kagome lattice with a high density of ligands and metal ions, which favours extended π-electron conjugation and strong π–d interactions. The result is well-dispersed electronic bands and narrow or even zero band gaps.[4]

Over the past decade, conductivity and charge carrier mobility of ECCPs have improved markedly, but their anisotropic charge transport, the dependence of conduction on the direction within the crystal, is still being explored.[4,7,8,9,10] A low-symmetry ECCP with in-plane electrical anisotropy had not been realized experimentally. The team set out to make one.

Synthesis and Structural Characterization of Cu_5BHT

The researchers grew Cu_5BHT on a water surface in a Langmuir trough, in four steps from the copper solution to the transfer of the film (Fig. 1a, 1b). The result was a black film of about 50 cm^2, visible to the naked eye. The box describes the recipe.

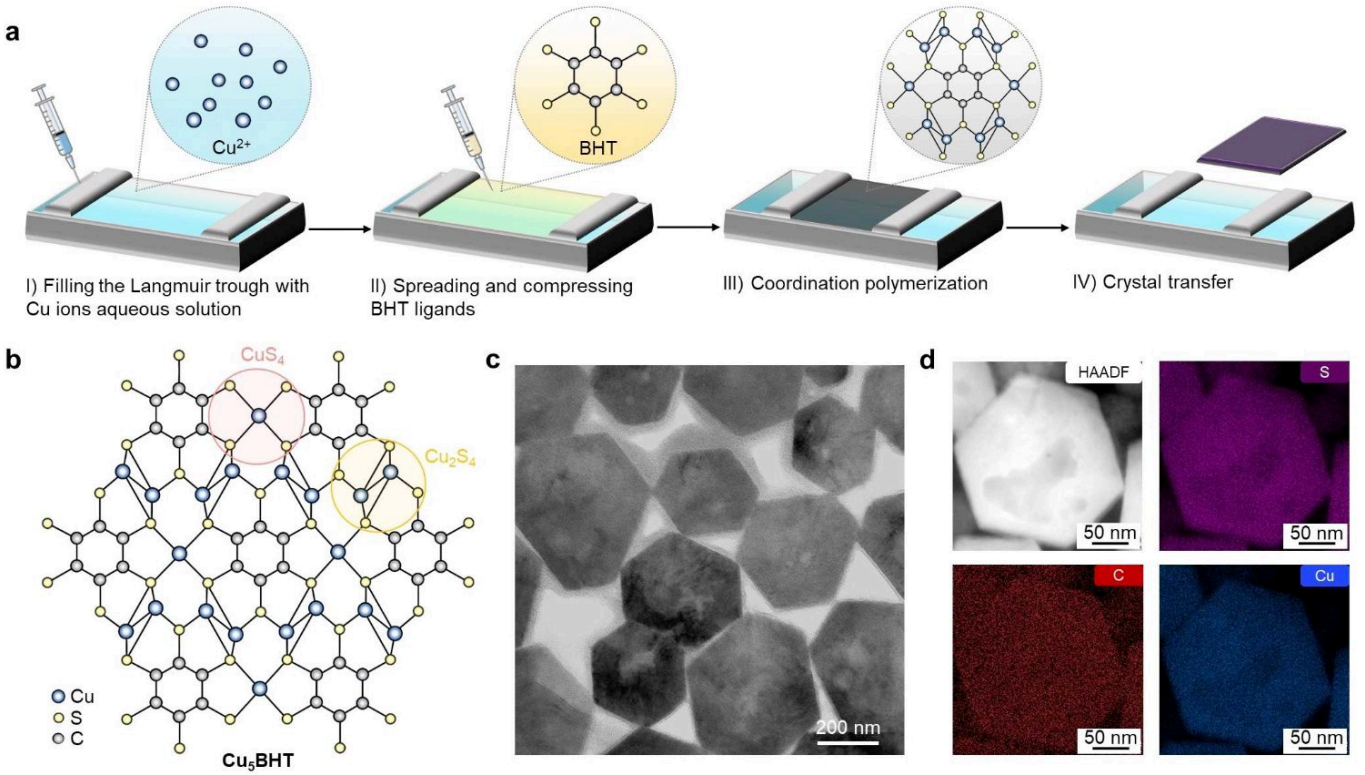

Fig. 1: Synthesis on the water surface (a), structure of Cu5BHT with its two building units (b), TEM image of the hexagonal crystals (c) and elemental maps (d).

Synthesis: Cu_5BHT on the water surface

First, a Langmuir trough was filled with an aqueous $Cu(NO_3)_2$ solution (about 2×10^{-4} M) as the subphase. Next, 150 µL of a freshly prepared solution of BHT (0.3 mg mL^{-1}) in a chloroform/*N*,*N*-dimethylformamide (DMF) mixture (2:1 v/v) was carefully spread onto the water surface and compressed. After 10 hours of coordination polymerization (step III), a black film with a lateral size of approximately 50 cm^2 covered the water surface. With the horizontal dipping method, the team transferred the film onto various substrates, including Si/SiO_2 and copper grids, for morphological and structural analysis.

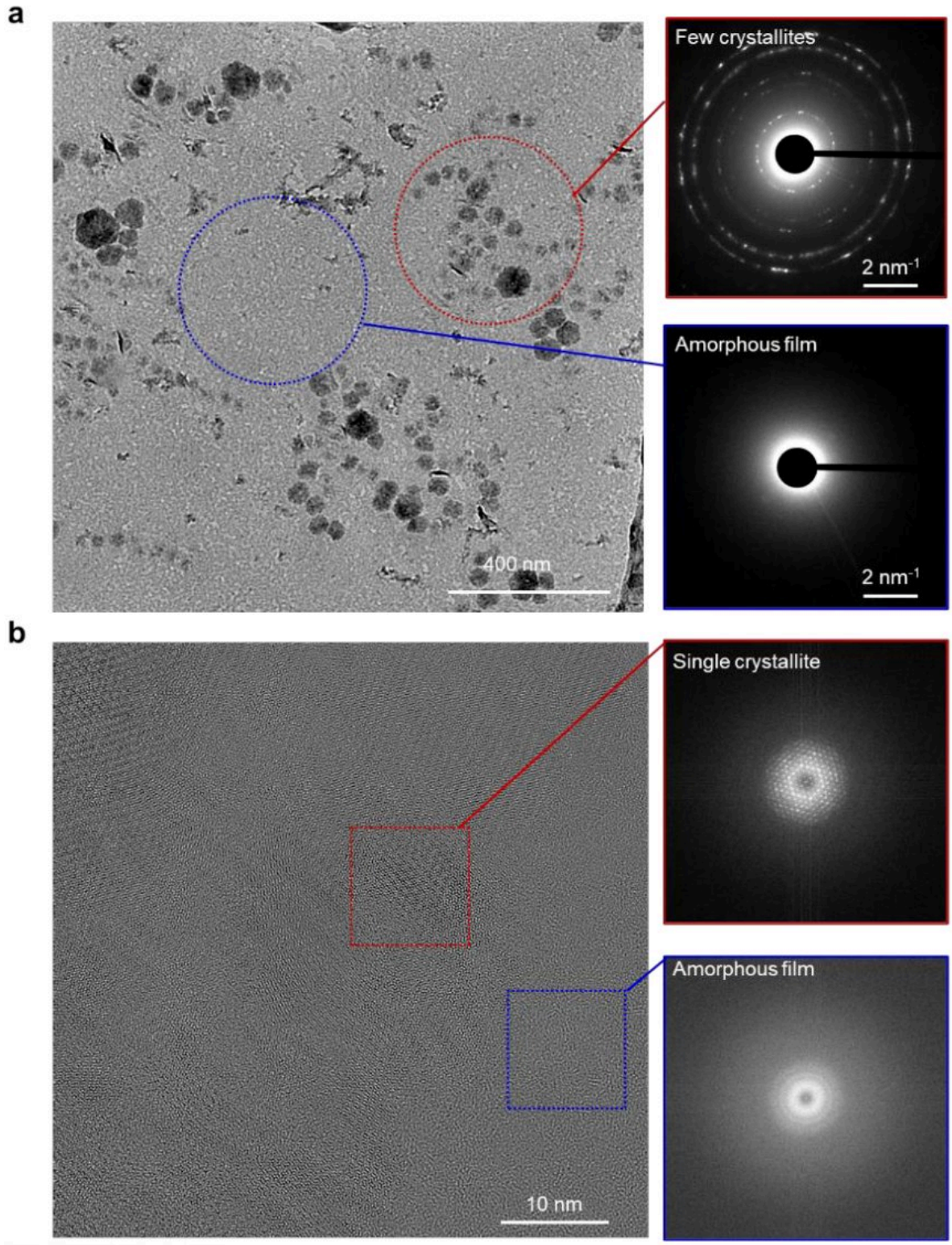

Fig. 2: Electron diffraction (a) and AC-HRTEM with FFT (b) of crystallites and the amorphous film between them.

Transmission electron microscopy (TEM) showed that the film consists of densely packed crystal domains, interspersed with smaller crystallites and an amorphous thin film (Fig. 2). The main domains have an asymmetric hexagonal shape with lateral dimensions from 200 nm to 1 µm (Fig. 1c). Elemental mapping by energy-dispersive X-ray spectroscopy in the scanning TEM

(STEM-EDX) confirmed a uniform distribution of carbon, sulfur and copper across the entire domain (Fig. 1d).

Crystallographic Analysis and Phase Purity

A low-magnification TEM image shows an asymmetric hexagonal Cu_5BHT flake (Fig. 3a). Selected-area electron diffraction (SAED) recorded perpendicular to the crystal surface gave sharp spots, indicating a single crystal, arranged in a hexagon whose angles are not all 120° (Fig. 3b). These unequal angles point to a low-symmetry lattice. The first-order spots lie at 1.35 nm^{-1}, corresponding to a lattice spacing of 7.4 Å.

To reach higher spatial resolution while keeping radiation damage low, the team used low-dose aberration-corrected high-resolution TEM (AC-HRTEM) at 80 kV with a dose rate of 3.2×10^3 e^- $Å^{-2}$ s^{-1}. The image in Fig. 3c shows well-aligned Kagome-like lattices without noticeable defects or domain boundaries, in excellent agreement with the crystal structure of Cu_5BHT. The measured lattice distance of 7.4 Å matches the SAED value.

In the magnified image, individual atomic positions are clearly resolved. They reveal an asymmetric structure made of two kinds of secondary building units (SBUs): square-planar CuS_4 and non-planar Cu_2S_4, which differ in the contrast of their copper atoms (Fig. 3d, 3e). According to the study, the Cu_2S_4 units form layers along the (110) and (1-10) crystal directions, connected by chains of alternating benzene rings and CuS_4 units along the (010) direction.

Fast Fourier transforms (FFT) of the AC-HRTEM images showed the same distorted six-fold pattern as the SAED (Fig. 4). This identified the longest diagonal of the hexagonal crystals as the (010) direction; it lies between the two angles of less than 120°.

X-ray scattering on a macroscopic film confirmed the structure (Figs. 3f, 3g); the box gives the details. Cu_5BHT crystallizes in the orthorhombic P2gg space group with the unit cell parameters *a* = 14.69 Å, *b* = 8.48 Å and *c* = 3.45 Å. Simulated AC-HRTEM images, SAED patterns and projection profiles agreed excellently with the experiment and confirmed the phase purity of Cu_5BHT (Fig. 3e). From these results, the team built an atomic model for density functional theory (DFT) calculations, which shows a distinct local structure of low symmetry (Fig. 3h).

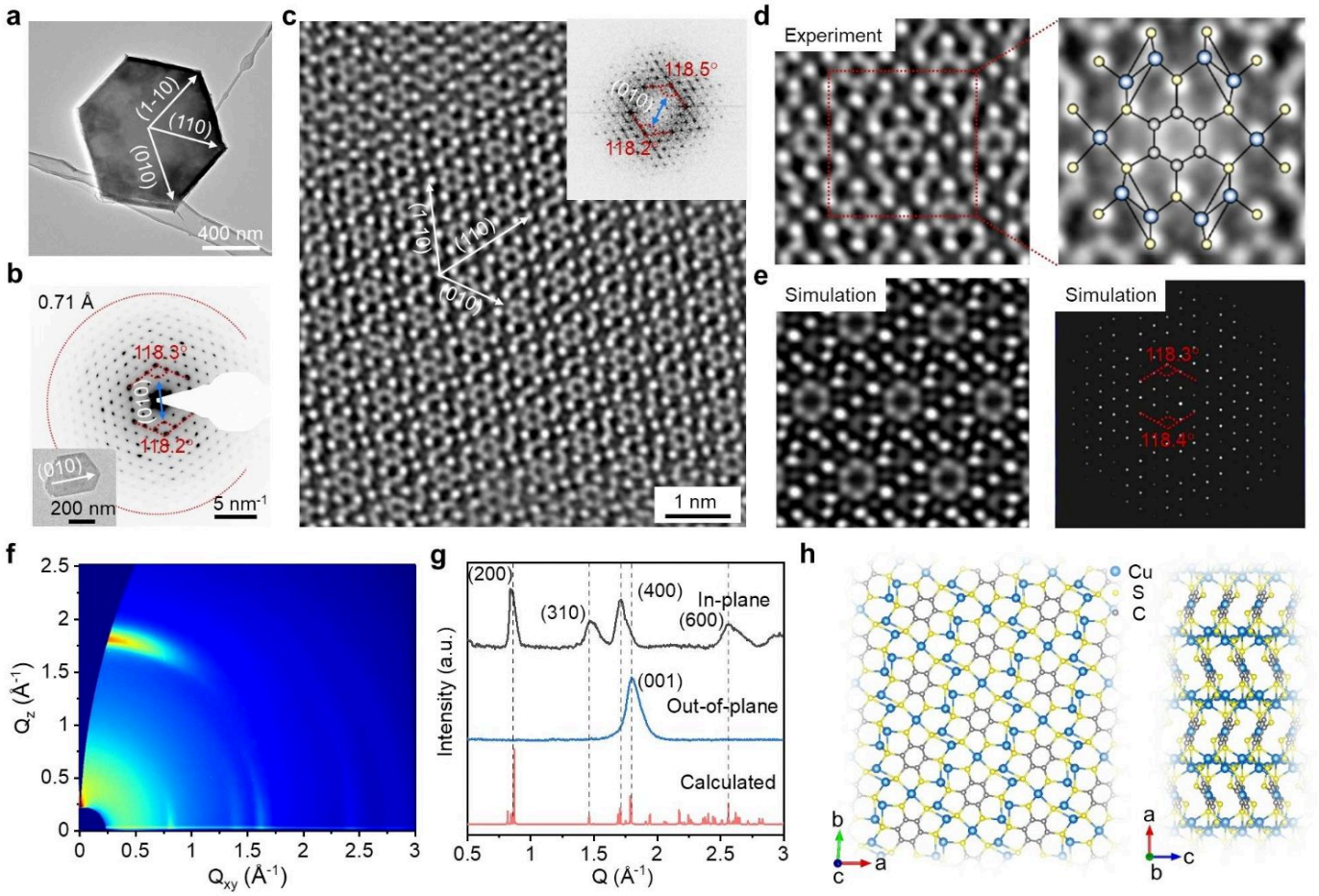

Fig. 3: TEM (a) and electron diffraction (b) of a crystal, AC-HRTEM image (c), magnified image with model (d), simulations (e), X-ray scattering (f, g) and crystal structure (h).

X-ray scattering: GIWAXS on a Cu_5BHT film

The grazing-incidence wide-angle X-ray scattering (GIWAXS) pattern of a 100 nm thick film on silicon shows discrete Bragg spots near Q_z = 0, indicating high crystallinity on a macroscopic scale (Fig. 3f). The in-plane peaks at Q_{xy} = 0.86, 1.49, 1.72 and 2.56 $Å^{-1}$ correspond to the (200), (310), (400) and (600) reflections, with a *d*-spacing of 7.3 Å (Fig. 3g), consistent with AC-HRTEM and SAED.

An intense arc at 1.82 $Å^{-1}$ indicates an interlayer stacking distance of about 3.45 Å and shows that the layers lie preferentially face-on, parallel to the substrate.

Chemical Stability and Charge Transfer Mechanism

In Cu_5BHT, copper is present as Cu^+, although the synthesis starts from Cu^{2+}. The reduction is likely driven by electron transfer from sulfur. The crystals also proved chemically and thermally robust. The box below explains both; Figs. 5 and 6 are inside the box.

Chemistry: copper oxidation state and stability

The formation of Cu_5BHT proceeds in three steps. First, Cu^{2+} reacts with a thiol to form a Cu^{2+}–thiol complex. Electron transfer from the thiol then yields Cu^+ and a thiol radical.[11,12] Finally, Cu^+ reacts with a second thiol to form a $(Cu^+)_2$ cluster–thiol or Cu^+–thiol complex. Peak deconvolution of the S 2s spectrum shows that the CuS_4 and Cu_2S_4 moieties carry oxidation states of –1 and 0 in a ratio of 31:69,[13] consistent with a CuS_4:Cu_2S_4 ratio of 1:2.

TEM and SAED showed that the crystals keep their structure and crystallinity after 12 hours in organic solvents and after annealing at 300 °C under nitrogen for 12 hours (Fig. 5).

X-ray absorption spectra at the Cu K-edge compare Cu_5BHT with copper foil, CuS and Cu_2S (Fig. 6a). The extended X-ray absorption fine structure (EXAFS) shows a Cu^+–S peak at 1.85 Å that matches Cu_2S rather than the Cu^{2+}–S peak of CuS, and a second peak at 2.31 Å from Cu–Cu interactions within the Cu_2S_4 units (Fig. 6b, 6c).[14]

Electronic Properties and In-Plane Anisotropic Conductivity

According to the theoretical calculations, Cu_5BHT is a metal, and its structure itself predicts a preferred direction: well-conducting chains of CuS_4 units run through slabs of less-conducting Cu_2S_4 units, all oriented along one crystal direction.

To test this on single crystals, the team connected crystals to Cr/Au electrodes with platinum wires written by a helium ion beam (Fig. 7a). Compared with conventional gallium ion beams, helium ions offer higher resolution and damage the sample less. Linear four-point-probe (4pp) current–voltage curves showed Ohmic contacts (Fig. 7b), consistently at all six electrode–polymer interfaces.

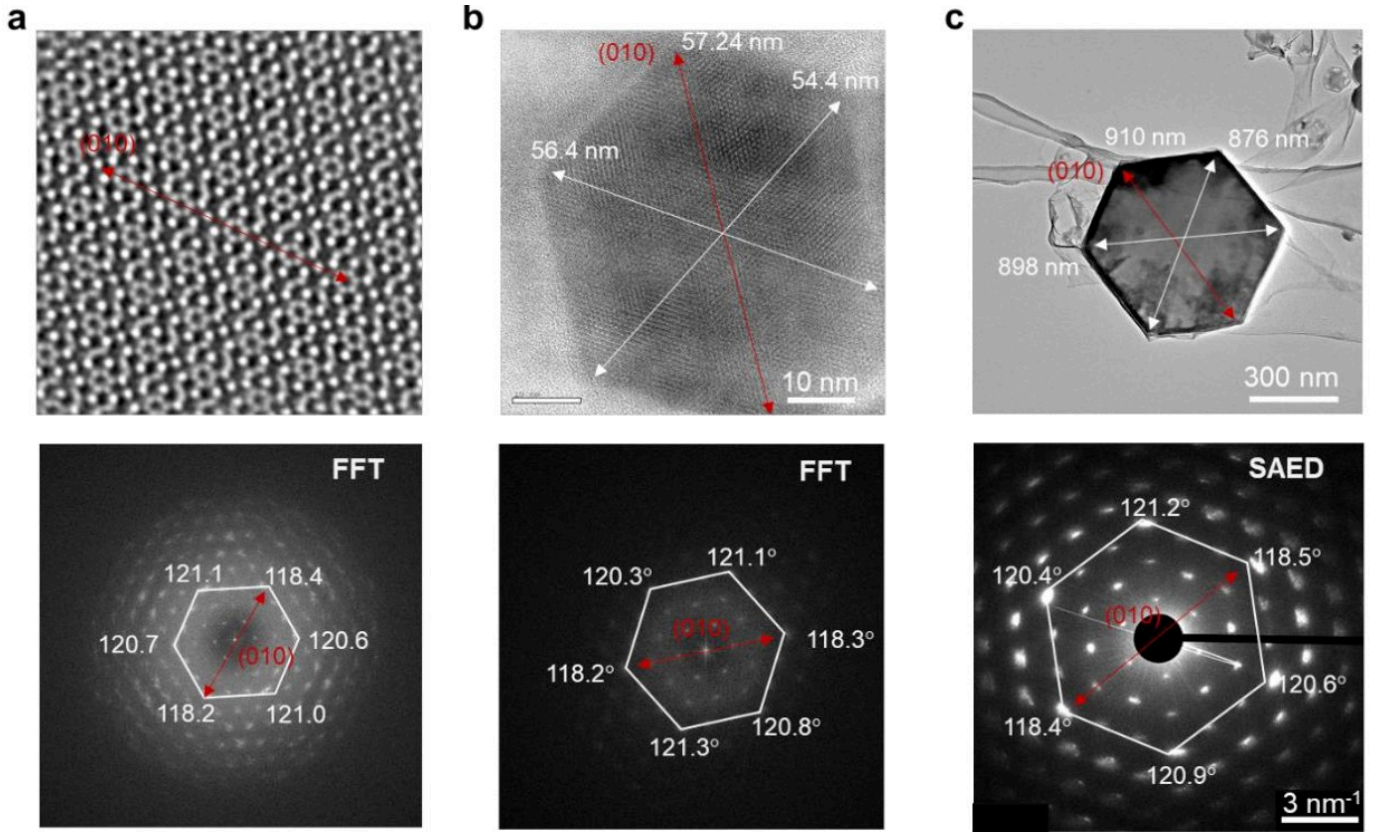

Fig. 4: AC-HRTEM images with FFT (a, b) and a single crystal with its diffraction pattern (c); red arrows mark the (010) direction.

Between 300 and 30 K, the conductance increased monotonically on cooling along all three crystal directions, (010), (110) and (1-10) (Fig. 7c), a hallmark of metallic behaviour. At room temperature, the conductance along (010) exceeded that along (110) and (1-10) by an anisotropic factor, $A = \sigma_{(010)}/\sigma_{(110)}$ or $\sigma_{(010)}/\sigma_{(1\text{-}10)}$, of about 8 (Fig. 7c, inset), and the factor grew further on cooling. The order $\sigma_{(010)} > \sigma_{(110)} \approx \sigma_{(1\text{-}10)}$ agrees with the theoretical predictions and is the first experimental demonstration of in-plane electrical anisotropy in a low-symmetry ECCP. For the other Cu_xBHT phases (x = 3, 4, 5.5), no comparable anisotropy has been observed at the device level.

The study shows that the same ingredients, copper and BHT, can form a new, low-symmetry network whose structure fixes the direction of current flow. “This work demonstrates a novel low-symmetry ECCP and highlights its potential for achieving in-plane electrical anisotropy,” the authors conclude. Direction-dependent conductors are of interest for electronic components that exploit anisotropy, as in inorganic 2D materials such as ReS_2, where anisotropic transistors have already been combined into digital inverters.[10] The atomic structure behind the effect was resolved by low-dose aberration-corrected HRTEM at Ulm University.

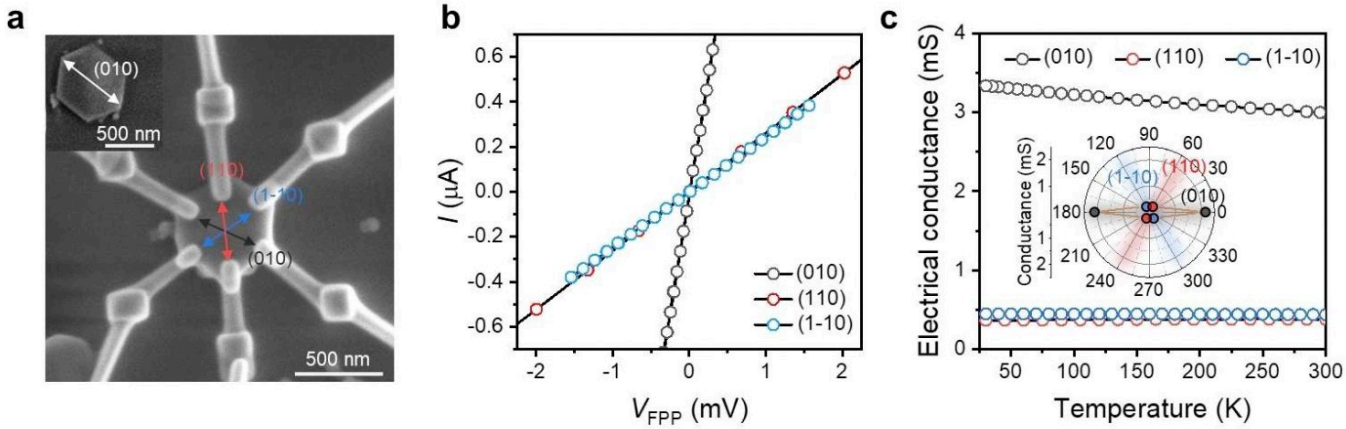

Fig. 7: Single-crystal device (a), current–voltage curves (b) and conductance versus temperature along three crystal directions (c).

Resource

Wang, Z., Un, H.-I., Liu, T.-J., Liang, B., Polozij, M., Hambsch, M., Pöhls, J. F., Weitz, R. T., Mannsfeld, S. C. B., Kaiser, U., Heine, T., Sirringhaus, H., Feng, X. & Dong, R. (2025).
A low-symmetry copper benzenehexathiol coordination polymer with in-plane electrical anisotropy.
Angew. Chem. Int. Ed., **64**(13), e202423341.
https://doi.org/10.1002/anie.202423341

References

1. Huang, X., Sheng, P., Tu, Z., et al. (2015). A two-dimensional π–d conjugated coordination polymer with extremely high electrical conductivity and ambipolar transport behaviour. *Nat. Commun.*, **6**, 7408. https://doi.org/10.1038/ncomms8408
2. Dou, J.-H., Sun, L., Ge, Y., et al. (2017). Signature of Metallic Behavior in the Metal–Organic Frameworks M_3(hexaiminobenzene)$_2$(M = Ni, Cu). *J. Am. Chem. Soc.*, **139**, 13608–13611. https://doi.org/10.1021/jacs.7b07234
3. Huang, X., Qiu, Y., Wang, Y., et al. (2020). Highly Conducting Organic–Inorganic Hybrid Copper Sulfides $Cu_xC_6S_6$ (x=4 or 5.5): Ligand-Based Oxidation-Induced Chemical and Electronic Structure Modulation. *Angew. Chem. Int. Ed.*, **59**, 22602–22609. https://doi.org/10.1002/anie.202009613
4. Wang, Z., St. Petkov, P., Zhang, J., et al. (2024). Benzenehexol-Based 2D Conjugated Metal–Organic Frameworks with Kagome Lattice Exhibiting a Metallic State. *Adv. Funct. Mater.*, **34**, 2404680. https://doi.org/10.1002/adfm.202404680
5. Chen, T., Dou, J.-H., Yang, L., et al. (2020). Continuous Electrical Conductivity Variation in M_3(Hexaiminotriphenylene)$_2$(M = Co, Ni, Cu) MOF Alloys. *J. Am. Chem. Soc.*, **142**, 12367–12373. https://doi.org/10.1021/jacs.0c04458
6. Huang, X., Fu, S., Lin, C., et al. (2023). Semiconducting Conjugated Coordination Polymer with High Charge Mobility Enabled by “4 + 2” Phenyl Ligands. *J. Am. Chem. Soc.*, **145**, 2430–2438. https://doi.org/10.1021/jacs.2c11511
7. Dou, J.-H., Arguilla, M.Q., Luo, Y., et al. (2021). Atomically precise single-crystal structures of electrically conducting 2D metal–organic frameworks. *Nat. Mater.*, **20**, 222–228. https://doi.org/10.1038/s41563-020-00847-7
8. Day, R.W., Bediako, D.K., Rezaee, M., et al. (2019). Single Crystals of Electrically Conductive Two-Dimensional Metal–Organic Frameworks: Structural and Electrical Transport Properties. *ACS Cent. Sci.*, **5**, 1959–1964. https://doi.org/10.1021/acscentsci.9b01006
9. Wang, Z., Walter, L.S., Wang, M., et al. (2021). Interfacial Synthesis of Layer-Oriented 2D Conjugated Metal–Organic Framework Films toward Directional Charge Transport. *J. Am. Chem. Soc.*, **143**, 13624–13632. https://doi.org/10.1021/jacs.1c05051
10. Liu, E., Fu, Y., Wang, Y., et al. (2015). Integrated digital inverters based on two-dimensional anisotropic ReS_2 field-effect transistors. *Nat. Commun.*, **6**, 6991. https://doi.org/10.1038/ncomms7991
11. Brust, M., Blass, P.M. & Bard, A.J. (1997). Self-Assembly of Photoluminescent Copper(I)–Dithiol Multilayer Thin Films and Bulk Materials. *Langmuir*, **13**, 5602–5607. https://doi.org/10.1021/la970493u
12. Daniel, T.A., Uppili, S., McCarty, G., et al. (2007). Effects of Molecular Structure and Interfacial Ligation on the Precision of Cu-Bound α,ω-Mercaptoalkanoic Acid “Molecular Ruler” Stacks. *Langmuir*, **23**, 638–648. https://doi.org/10.1021/la0621719

13. Karthikeyan, M., Bhagyaraju, B., Mariappan, C.R., et al. (2012). Novel semiconducting metal-organic framework: Synthesis, structural characterisation and electrical conductivity studies of manganese based two dimensional coordination polymer. *Inorg. Chem. Commun.*, **20**, 269–272. https://doi.org/10.1016/j.inoche.2012.03.024

14. Lin, S.-C., Chang, C.-C., Chiu, S.-Y., et al. (2020). Operando time-resolved X-ray absorption spectroscopy reveals the chemical nature enabling highly selective CO_2 reduction. *Nat. Commun.*, **11**, 3525. https://doi.org/10.1038/s41467-020-17231-3