

Microscopic origin of chiral shape induction in achiral crystals

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In biomineralization, inorganic materials are formed with remarkable control of the shape and morphology. Chirality, as present in the biomolecular world, is therefore also common for biominerals. Biomacromolecules, like proteins and polysaccharides, are in direct contact with the mineral phase and act as modifiers during nucleation and crystal growth. Owing to their homochirality—they exist only as one of two possible mirror-symmetric isomers—their handedness is often transferred into the macroscopic shape of the biomineral crystals, but the way in which handedness is transmitted into achiral materials is not yet understood at the atomic level. By using the submolecular resolution capability of scanning tunnelling microscopy, supported by photoelectron diffraction and density functional theory, we show how the chiral 'buckybowl' hemibuckminsterfullerene arranges copper surface atoms in its vicinity into a chiral morphology. We anticipate that such new insight will find its way into materials synthesis techniques.

Influencing the macroscopic shape of a crystal during growth requires molecular tectonics, that is, adsorbed molecules that arrange and stabilize new sites at the surface of the material¹. Today, crystallization at the crystal/liquid interface can be investigated at high resolution with scanning probe microscopy, but so far such studies have addressed only the growth of the mineral phase itself^{2,3}. Previous investigations addressed the reorganization of inorganic surfaces by achiral and chiral molecules^{4–7}. However, the microscopic role that molecules play during crystal growth, for example as surfactants at step edges, remains poorly understood^{8,9}. All the steps of crystal growth, including the adsorption of atoms or molecules from the liquid or gas phase onto the crystal surface, migration across the surface and along step edges, incorporation at kink or step sites and nucleation of new islands, are also available at the metal/vacuum interface. This opens up a way to study molecular tectonics and crystal growth with the high precision provided by scanning tunnelling microscopy (STM)¹⁰. The Cu(110) surface, with its high mobility of top-layer atoms at room temperature¹¹, provides an excellent model system for studying the initial steps of crystal shaping by molecules. To influence the morphology of the crystal significantly, the organic modifier needs to interact sufficiently with the inorganic material. For example, for calcite, the most-abundant biomineral, dicarboxylic acids have been identified as efficient modifiers, because both carboxylate groups interact strongly with calcium ions¹².

In the case of Cu, polar molecules, such as carboxylic acids, amino acids and chiral ketones, have been identified as suitable chiral modifiers for the induction of handedness into the crystal surface^{6,13–18}. However, as the binding configurations of the molecules at the kink sites are poorly resolved, a microscopic picture of chiral recognition and chiral crystal surface formation has not been obtained so far. Here we show that the aromatic chiral bucky-bowl hemifullerene (C₃₀H₁₂ (Fig. 1a)), representing half of a C₆₀

buckyball and lacking any functional groups, can also act as a crystal-shape modifier. We find that certain chiral kinks are stabilized by metal–organic coordination bonds, whereby opposite mirror isomers, so-called enantiomers, create opposite chiral kinks. In our work, the absolute handedness of the molecules is obtained with STM of submolecular resolution in combination with synchrotron radiation X-ray photoelectron diffraction (XPD), which discloses the orientation of the bowl at the chiral kink sites. The exact binding geometry of the chiral bucky-bowl at the kink is identified via density functional theory (DFT), which reveals that the chiral recognition of hemifullerene at the Cu(110) surface can be explained with the classic three-point contact model.

Results and discussion

After the deposition of ~15% of a close-packed monolayer of the racemic (1:1) mixture of minus (*M*) and plus (*P*) enantiomers¹⁹ at room temperature and cooling to 50 K, the Cu surface shows remarkable signs of restructuring. Step edges exhibit a pronounced sawtooth shape with straight segments parallel to the $[\bar{3}34]$ and $[\bar{3}34]$ directions of the surface plane (Fig. 1b). In addition, islands with an asymmetric shape appear on the terraces, with their edges also aligned along the $[\bar{3}34]$ and $[\bar{3}34]$ directions (Fig. 1c). Each of these directions breaks the mirror symmetry of the underlying Cu(110) surface, and all the step edges are decorated with hemifullerene molecules. Single hemifullerene molecules on the flat terraces are only observed at low temperatures (Fig. 1b), because they are too mobile at room temperature to be imaged by STM (Fig. 1c).

The asymmetric shape of the islands and the mirror-symmetry breaking direction of the step edges suggest an enantioselective decoration. That is, $[\bar{3}34]$ steps are decorated with one type of enantiomer and the $[\bar{3}34]$ steps with the other. Indeed, the equal STM appearance of molecules at the same type of step supports this conclusion. Very narrow elongated islands are also observed, which are

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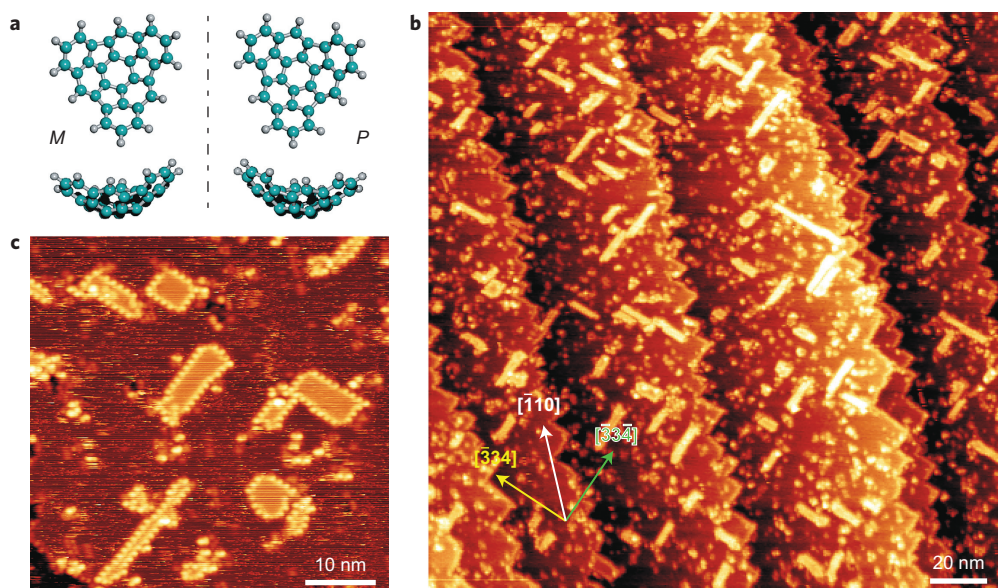


Figure 1 | Initial steps of chiral faceting of Cu(110) by hemifullerene. **a**, Ball-and-stick models of *M*- and *P*-hemifullerene ($C_{30}H_{12}$), looking towards their concave side. **b**, STM image ($U = -2.0$ V, $I = 22$ pA, $T = 50$ K) acquired after the deposition of 15% of a complete monolayer of hemifullerene at room temperature. Instead of linear step edges along $[110]$, as observed for clean Cu(110), the step edges are decorated with molecules and have a zigzag shape that exhibits $[\bar{3}\bar{3}\bar{4}]$ and $[\bar{3}\bar{3}\bar{4}]$ directions. On the (110) terraces, single molecules, nanowires and elongated islands with edges aligned along the $[\bar{3}\bar{3}\bar{4}]$ and $[\bar{3}\bar{3}\bar{4}]$ directions are observed. **c**, STM image ($U = -2.0$ V, $I = 23$ pA, $T = 300$ K) of a step-free surface region acquired at room temperature. Decorated two-dimensional (2D) islands are still observed on the terrace, with edges also running parallel to the $[\bar{3}\bar{3}\bar{4}]$ and $[\bar{3}\bar{3}\bar{4}]$ directions. Single molecules are not observed between the decorated islands, but streaky features indicate diffusing molecules.

decorated with one enantiomer only (Fig. 2a,c,d). Considering the C_3 symmetry of the hemifullerene molecules, it is not possible to assign the absolute handedness solely from STM. If the C_3 axis of the molecular bowl was normal to the surface, then the three uppermost C6 rings would be at identical heights above the surface and, hence, it would be impossible to determine the intrinsic handedness of a hemifullerene molecule via STM. However, all the molecules show a pronounced contrast in STM because of a tilted adsorption geometry. With the knowledge of the exact adsorption geometry, it therefore becomes possible to establish the handedness from STM. Detailed conclusions on the orientation of the molecules on the surface are achieved here with XPD²⁰. As XPD is an averaging technique for a larger surface area, both surface species—terrace and step-edge molecules—and their relative abundance need to be taken into account. Using the ratio of step and terrace molecules at a given coverage—obtained by counting the molecules in large-scale STM images—the best fit to the XPD pattern is obtained with a tilt of the molecular C_3 axis away from the surface normal by 10° at the terrace and 18° at the step edge (Supplementary Figs 1–3; for details on the XPD data analysis see the Supplementary Information).

With the knowledge of the adsorbate geometry, in particular the polar tilt angle and the tilt direction of the molecular bowl, the STM appearance can be modelled and compared with the experimental results (Fig. 2). As previously observed for the bucky-bowl corannulene^{21,22}, hemifullerene interacts with its convex side with the Cu surface. On flat terraces, three bright lobes in the STM appearance of a single molecule coincide with the three outer C6 rings (Fig. 2e–g). The different intensities of the lobes when imaged reflects that the molecule is slightly tilted by 10° (Fig. 2h). This allows the determination of the molecular handedness by modelling the STM appearance for a given tilt of the C_3 axis of the bowl (Fig. 2g). A clockwise height decrease of the three C6 rings identifies an *M* enantiomer (Fig. 2g), whereas an anticlockwise height decrease is assigned to the *P* enantiomer (see Supplementary Fig. 1). However, the adsorption geometry at the step edge differs substantially from that on the terraces. As a

result of the larger tilt of the molecular bowl of 18° along a different direction (see Supplementary Fig. 1), the height-decrease sequence of the three outer C6 rings turns in the opposite sense for the same enantiomer at the step edge with respect to the situation on the flat terrace. The *M* enantiomer shows, for example, a clockwise contrast sequence on the terrace (Fig. 2e–h), but an anticlockwise contrast sequence at the step edge (Fig. 2i–l). For the correct assignment of the contrast sequence of molecules that are not isolated, for example, molecules that decorate a step edge in a single line, we started the analysis at the end of the line (corner molecule) to make sure that only lobes from the same single molecule were evaluated. Altogether, such a detailed contrast analysis of this complex situation reveals that step edges running parallel to the $[\bar{3}\bar{3}\bar{4}]$ direction are decorated exclusively with *M* enantiomers and step edges running parallel to the $[\bar{3}\bar{3}\bar{4}]$ direction are decorated only with *P* enantiomers (for details, see Supplementary Fig. 4).

Molecular and stereoselective recognition at crystal surfaces has been known for some time^{23–25}, and that enantiomers bind preferentially to chiral kinks has been shown before^{26–31}. By contrast, here the chiral kinks are created by a chiral molecule. A step edge running along the $[\bar{3}\bar{3}\bar{4}]$ direction has chiral *R* kinks; the one running along the $[\bar{3}\bar{3}\bar{4}]$ direction has *S* kinks (Fig. 3). With a kink periodicity of 1.053 nm they basically span over two close-packed Cu rows of this (110) surface. For stepped and kinked face-centred cubic crystal surfaces, special notations have been proposed³². The *R/S* denominators for the handedness of kinks are based on the clockwise or anticlockwise sequences of (100), (110) and (111) facets at the kink, which involve a lower terrace facet (Supplementary Fig. 5)²⁶. From this it follows that *M*-hemifullerene creates *R* kinks and *P*-hemifullerene creates *S* kinks.

To understand how the molecule creates a chiral kink, the exact bonding situation at the kink was evaluated with DFT calculations. The most stable adsorption configurations of *M* enantiomers at the *R* and *S* kinks were searched by simulated annealing molecular dynamics calculations (see Methods for details). After geometrical optimization, the *M* enantiomer at the *R* kink site is, indeed, found

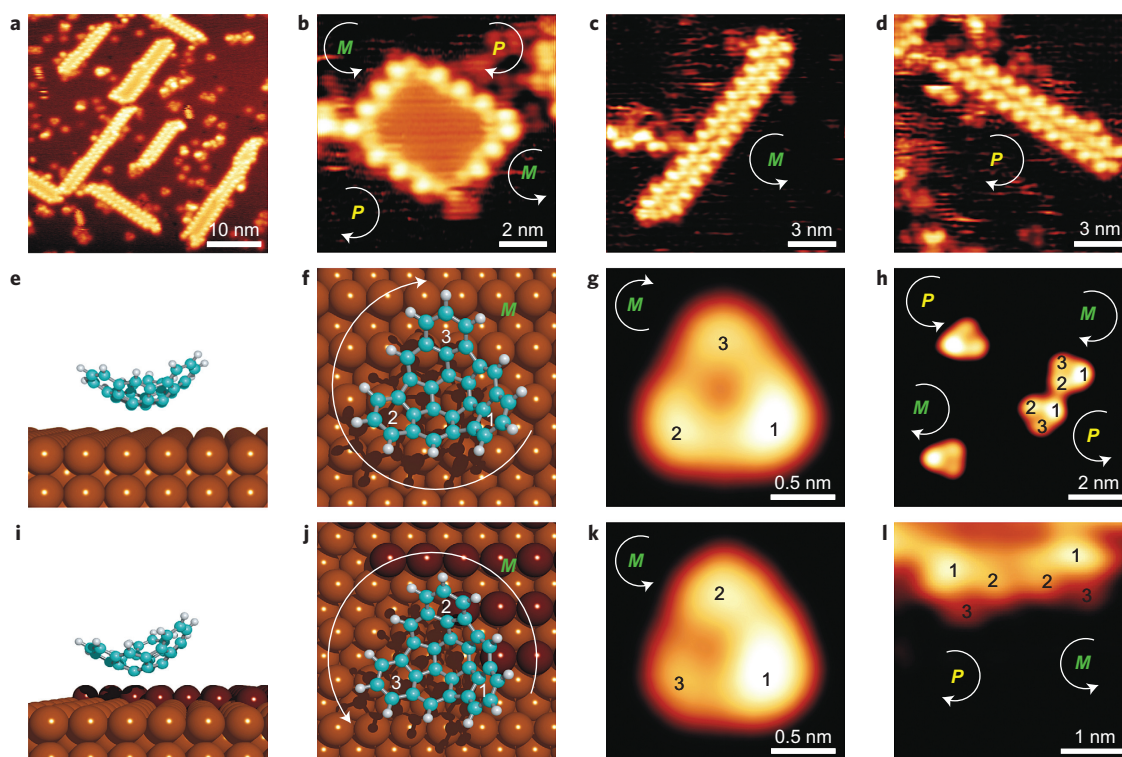


Figure 2 | Determination of the absolute handedness of hemifullerene molecules. **a**, STM image showing elongated islands decorated with hemifullerene molecules and single hemifullerene molecules on the flat terrace ($T = 50$ K, $U = -2.3$ V, $I = 23$ pA). **b-d**, Enantioselective step decoration of 2D Cu islands and Cu metal wires. Steps and wires running parallel to the $[\bar{3}34]$ direction are decorated with *M* enantiomers, and those running parallel to the $[\bar{3}\bar{3}4]$ direction are decorated with *P* enantiomers ($T = 300$ K, $U = -2.0$ V, $I = 23$ pA for **b**, and $U = -2.4$ V, $I = 35$ pA for **c** and **d**). **e, f**, Side and top views of the best-fit molecular orientation of *M*-hemifullerene on the terrace, as obtained from XPD. The molecular C_3 axis is inclined by 10° with respect to the surface normal. The heights of the C6 rings above the surface plane are marked as highest (1), middle (2) and lowest (3), which give rise to the different intensities of the three protrusions observed in STM images. **g**, Simulation of the STM appearance of a molecule on the flat terrace. With the knowledge of the tilt angle, the absolute handedness is determined from the sequence of intensity (highest to lowest) of the three lobes. **h**, STM image showing individual hemifullerene molecules on a flat Cu(110) terrace, and the assignment of their handedness ($T = 50$ K, $U = -2.32$ V, $I = 30$ pA). **i, j**, Side and top views of the molecular orientation of *M*-hemifullerene at a step edge, as obtained from XPD. The molecular C_3 axis is inclined by 18° with respect to the surface normal. **k, l**, Simulation of STM appearance of an *M*-enantiomer located at a step edge and an STM image ($U = -2.2$ V, $I = 23$ pA) showing both enantiomers at a corner of a 2D island.

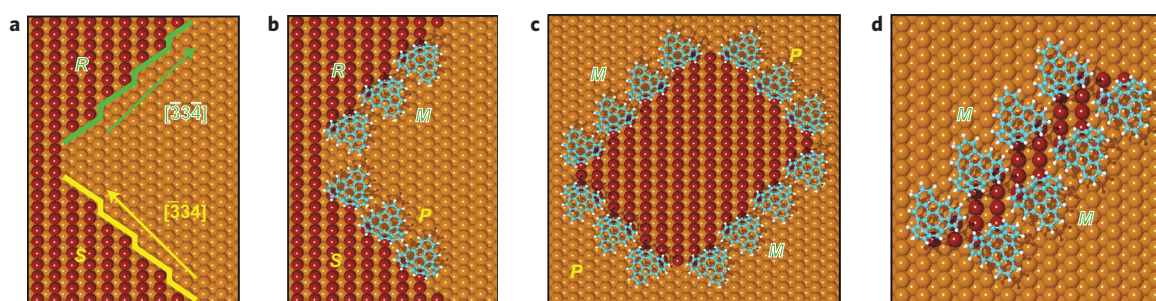


Figure 3 | Structure models for homochiral step edges. **a**, Hard-sphere model of the observed step edge with alternating $[\bar{3}\bar{3}4]$ and $[\bar{3}34]$ segments and the formation of chiral kink sites. **b**, Structure model of the observed hemifullerene-decorated steps along $[\bar{3}\bar{3}4]$ and $[\bar{3}34]$. *M* enantiomers decorate *R* kinks, and *P* enantiomers decorate *S* kinks. **c**, Structural model of an adatom island stabilized by *M*- and *P*-hemifullerene. **d**, Structural model of an *M*-hemifullerene-stabilized Cu adatom nanowire running along the $[\bar{3}\bar{3}4]$ direction.

to be the most favourable configuration (for a comparison of the configurations determined from DFT and from the XPD analysis, see Supplementary Fig. 6). Or, in other words, *M*-hemifullerene can only stabilize an *R* kink Cu atom at the upper step because of such a bonding configuration. With a total binding energy of 4.66 eV, the adsorbate is stabilized by 0.14 eV over the lowest energy configuration of an *M*-hemifullerene located at an *S* kink site (see Supplementary Fig. 7), and by 0.5 eV over a *M*-hemifullerene at a

straight step edge (see Supplementary Fig. 8). This energy difference is at the upper level of previously reported values of enantioselectivity (0.01 to 0.14 eV) for chiral kink adsorption^{28–31}, whereby the largest experimental values do not exceed 0.04 eV (refs 33,34).

The nature of the chemical bonding was evaluated with a distribution analysis of the charge-density difference (Fig. 4d–f). This procedure reveals that chiral kink creation is driven by three η^1 -coordinated Cu–C bonds, that is, a single bond is formed between a Cu

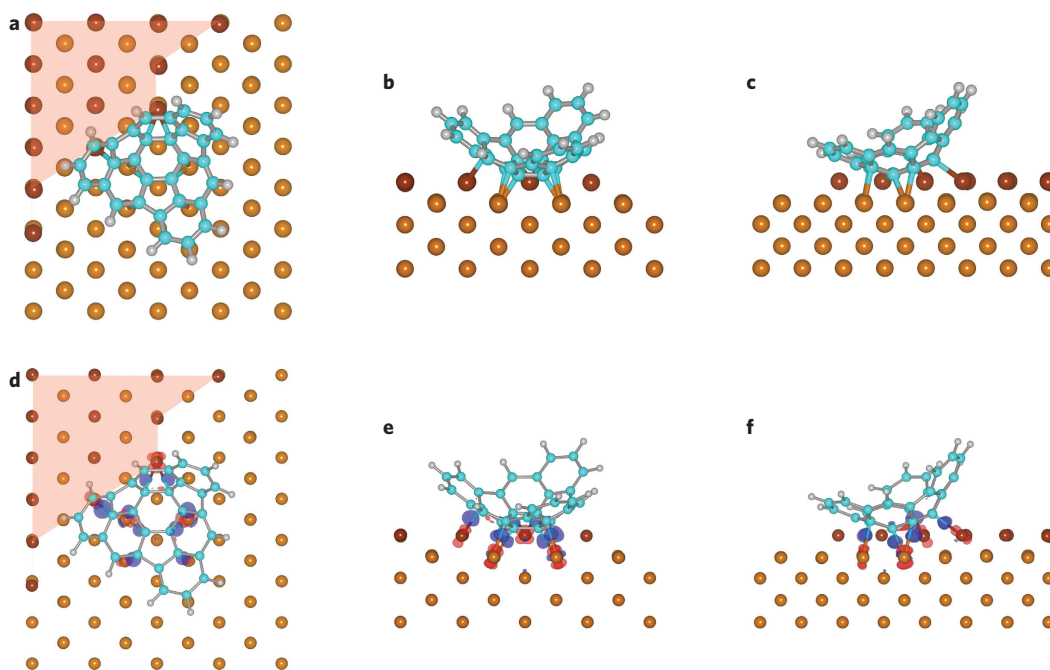


Figure 4 | Single *M*-hemifullerene-(-*R*)-kink complex. **a–c**, Top (**a**), front (**b**) and side (**c**) views of *M*-hemifullerene bound to an *R* kink as obtained by DFT calculations. Cu atoms of the lower terrace appear light brown, and Cu atoms of the upper terrace appear dark brown. **d–f**, The bonds are identified via calculations of the charge-density distribution. Charge depletion is marked in red, and charge accumulation in blue with a contour value of $0.06 \text{ e } \text{\AA}^{-3}$. Chirality transfer from the molecule to the metal arises via three η^2 - and three η^1 -coordinative bonds to Cu atoms of the metal substrate. One of each type of bond goes to kink atoms, and the others to atoms located in the lower terrace.

surface atom and a C atom, and three η^2 -coordinated Cu–C bonds, that is, each bond goes from a single Cu atom to two adjacent C atoms of the molecule (Fig. 4 and Supplementary Fig. 9). The six C atoms involved in the three η^2 bonds are all located in the central C6 ring of the hemifullerene, from which one of the η^2 bonds goes to the kink atom. The two other η^2 bonds go to adjacent Cu atoms on the lower terrace. A similar two-Cu-atom binding site in the lower terrace establishes two η^1 bonds to C atoms in the same C5 ring (labelled 2 and 3 in Supplementary Fig. 9a), whereas the remaining η^1 bond goes to a step-edge atom next to the kink atom. All the bond lengths are between 2.11 and 2.27 Å. The four Cu atoms of the binding site on the lower terrace represent a single (110) surface unit cell. When viewed from above, the sequence going from this terrace site via the step-binding site to the kink atom is clockwise for the *M*-hemifullerene/*R*-kink complex, but anticlockwise in the case of the *P*-hemifullerene/*S*-kink complex. Hence, these three mirror-like binding sites involved in the chiral recognition of hemifullerene at the Cu(110) surface are a manifestation of the classic three-point contact model of chiral recognition³⁵. The relatively strong Cu metal–fullerene interaction leads to the effect that at room temperature diffusing Cu atoms are captured by the hemifullerene molecules and the surface becomes restructured in the observed manner. This also leads to the formation of homochiral hemifullerene-stabilized adatom wires. Adsorption of only one enantiomer would lead to single-handed structures and to the stabilization of only one type of nanowire or handed material. For the particular case of hemifullerene, however, unfortunately all our attempts to separate the enantiomers have been unsuccessful so far.

Conclusions

In conclusion, we have shown under abiotic conditions and using submolecular-resolution STM, XPD and DFT calculations that the chiral geodesic hydrocarbon hemibuckminsterfullerene restructures a metal surface in such a way that chirality is imprinted onto the

metal. Such a restructuring can be considered as the first step towards the modification of achiral crystals into a chiral shape. At the microscopic level, chiral recognition occurs here via metal–organic coordination bonding between Cu atoms near step edges and specific molecular binding sites. Mobile Cu adatoms are immobilized into homochiral nanowires or chiral islands. Although a special example of the restructuring of a crystal (aromatic molecule and metal), our example here involves the elementary processes, such as the formation of kinks and chiral recognition at surfaces, that are of paramount importance for shape induction in biomineralization. Beyond step-edge propagation and step-edge morphology, previously studied for biominerals with scanning probe microscopy, our work now also gives a detailed insight into the interplay between the molecular modifier and the inorganic mineral phase.

Methods

Hemifullerene was synthesized according to the method of Scott *et al.*³⁶. Experiments were carried out in two independent ultrahigh vacuum systems. The variable-temperature STM system (Omicron Nanotechnology) was equipped with low-energy electron diffraction (LEED) and standard surface-preparation facilities. The Cu(110) single crystal was prepared by repeated cycles of sputtering with argon ions (typically at an argon pressure of 2×10^{-5} mbar and an acceleration voltage of 1.5 kV), and annealing at ~ 700 K. Before the deposition of hemifullerene, the cleanliness and surface order were checked by LEED and STM. Hemifullerene was sublimated from a Knudsen-cell type evaporator at a temperature of 480 K, with the Cu(110) substrate held at room temperature. STM images were acquired in constant-current mode either at room temperature or at a sample temperature of ~ 50 K. The XPD experiments were performed at the NearNode Endstation of the Surface and Interface Microscopy Beamline of the Swiss Light Source using linearly polarized synchrotron X-ray radiation of 920 eV. The C 1s ($E_{\text{kin}} = 626$ eV) XPD patterns were collected with the sample held at room temperature. Single-scattering cluster (SSC) simulations were used to find the molecular orientation that yields the lowest reliability factor (*R* factor) and hence the best agreement with experiment^{37,38}. Backscattering from the substrate atoms was neglected because the backscattering yield is very low within the kinetic-energy range used for this work (>400 eV).

DFT calculations were performed using the Vienna *ab initio* simulation package³⁹ in a generalized gradient approximation⁴⁰. The projector-augmented wave method was employed⁴¹. The van der Waals interactions were described by the method of Tkatchenko and Scheffler⁴², which significantly improves the accuracy for aromatic

molecules on metal substrates⁴³. The periodic slab models include four Cu layers, a kinked step, the *M* enantiomer of hemifullerene (a total of 161 atoms) and a vacuum layer larger than 19 Å. The most-stable adsorption configurations of *M*-hemifullerene at different kinked steps were searched by the simulated annealing method⁴⁴ based on molecular dynamics calculations⁴⁵, which is widely used in structure prediction without requiring reasonable structural inputs but relying on temperature evolution in time^{46,47}. The annealing starts with configurations far from equilibrium. The systems were then cooled down from 300 K to 0 K in 9 ps with 2 fs time steps and further relaxed at 0 K. The slow annealing process allows the molecule to cover a sufficiently large phase space and to find the most-stable adsorption configuration. In the optimization process, the bottom three Cu layers were frozen. The surface Cu layer, the kinked step-edge atoms and the molecule were fully relaxed until the residual forces were less than 0.015 eV Å⁻¹. A 400 eV energy cutoff for the plane-wave basis sets and Γ -point *k*-sampling in reciprocal space were used.

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Author contributions

R.F. and K.-H.E. conceived the experiments. W.X., T.G. and R.F. performed the experiments and data analysis. K.P., Y.Z., E.B. and W.A.H. conducted the theoretical modelling. L.P. and L.T.S. conducted the chemical synthesis. W.X., K.-H.E. and R.F. wrote the manuscript with contributions from all the authors.

Additional information

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Competing financial interests

The authors declare no competing financial interests.