
Supplementary information

Narrow carbon pentaheptite nanoribbon as a covalent metal

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Supplementary Information for

Narrow carbon pentaheptite nanoribbon as a covalent metal

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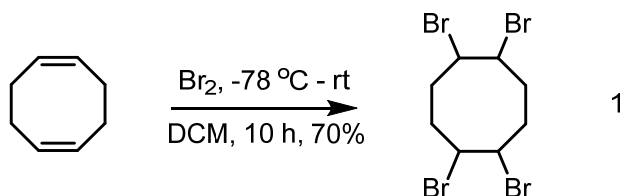
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Supplementary Methods

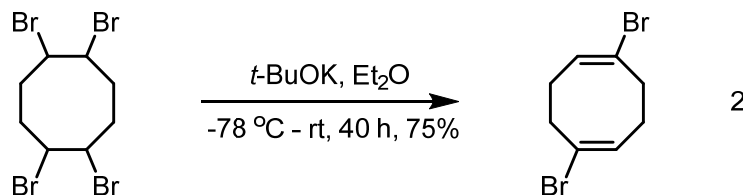
The synthesis of 1,5-dibromo-1,5-cyclooctadiene (DBCOD) was performed via solution-phase chemistry following the procedure reported in previous work¹, as detailed below.

Synthesis of 1,2,5,6-tetrabromocyclooctane (**1**).



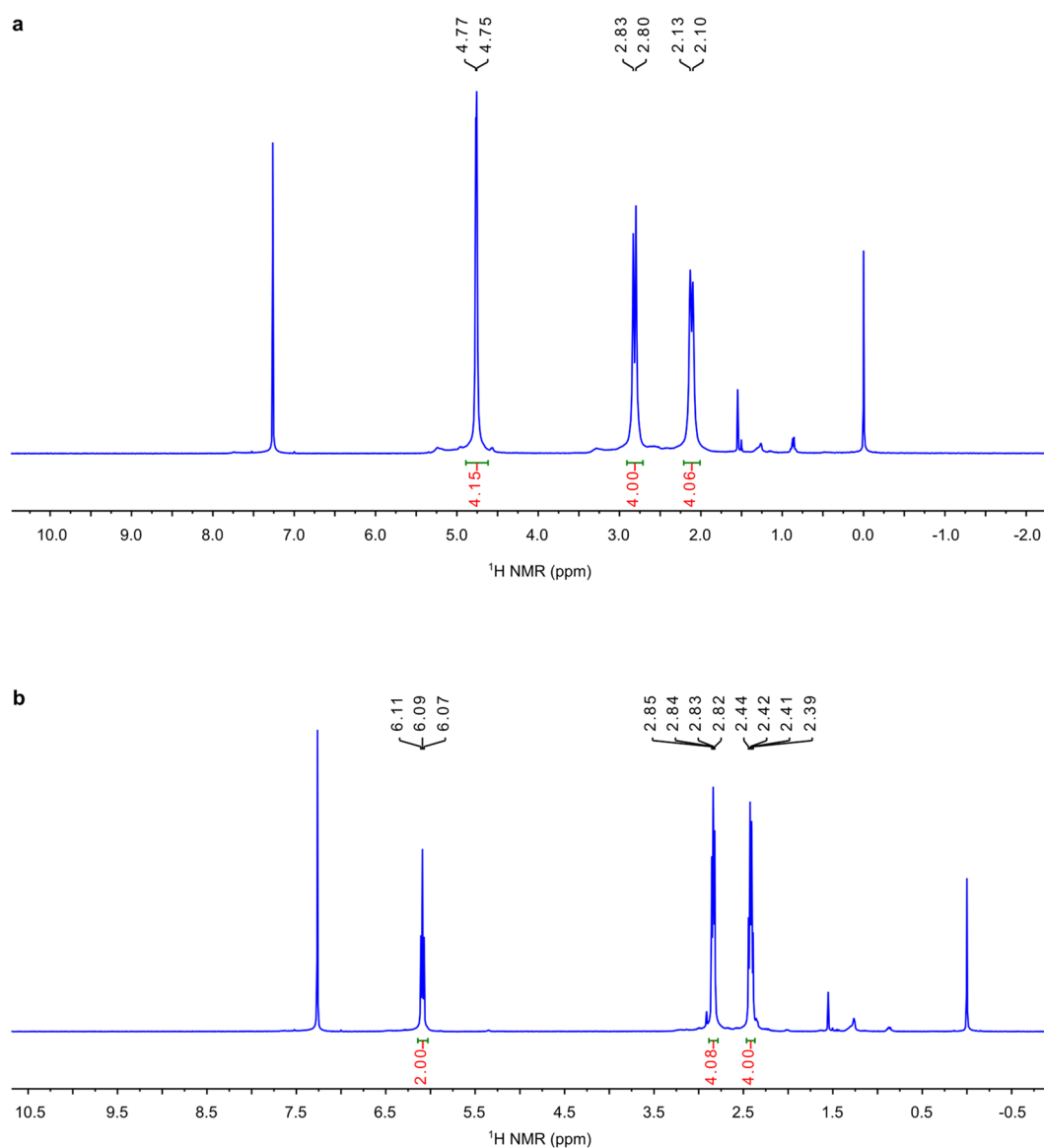
1,5-cyclooctadiene (1.10 g, 10.00 mmol, 1.00 equiv.), 4A molecular sieve and dichloromethane (35 mL) were added in a 100 mL three-mouth bottle. The reaction bottle was stirred at $-78\text{ }^\circ\text{C}$, then slowly added the dichloromethane solution of liquid bromine, and continued stirring for 15 minutes after the drip was finished. Then, the reaction temperature is slowly raised to room temperature and continue stirring overnight. After the reaction, it was quenched with saturated sodium sulfite solution, extracted with CH_2Cl_2 , the combined organic layers were washed with water, dried over MgSO_4 , concentrated, and recrystallized to obtain 1,2,5,6-tetrabromocyclooctane (**1**) (1.5 g, 70%). $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 4.76 (d, $J = 4.7\text{ Hz}$, 4H), 2.82 (d, $J = 13.4\text{ Hz}$, 4H), 2.11 (d, $J = 13.6\text{ Hz}$, 4H) was measured, as given in Supplementary Fig. 1a.

Synthesis of 1,5-dibromo-1,5-cyclooctadiene (**2**).



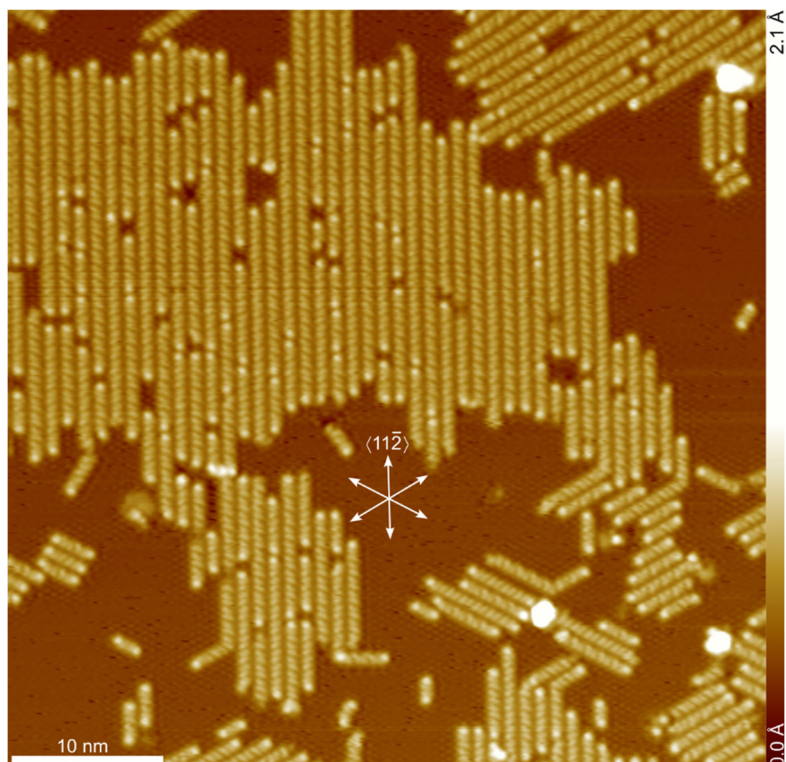
1,2,5,6-tetrabromocyclooctane (428 mg, 1.00 mmol, 1.00 equiv.) and KO^tBu (448 mg, 4.00 mmol, 4 equiv.) were mixed in a round-bottomed flask and cooled to $-78\text{ }^\circ\text{C}$ under nitrogen atmosphere. Diethyl ether (25 mL) was added to the mixture while stirring. The resulting suspension was allowed to warm to room temperature and was stirred until completion of the reaction (40 h), at which point a saturated aqueous solution of NH_4Cl and water were added and stirring was continued for a further 10 min. The resulting layers were separated, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were dried over MgSO_4 , filtered and the crude product was concentrated onto silica and purified on a short column using hexane as the eluent. The product consists of two isomers, product **2** (134 mg, 75%) was obtained through recrystallization. $^1\text{H NMR}$

(400 MHz, Chloroform-d) δ 6.09 (t, $J = 7.1$ Hz, 2H), 2.89 – 2.79 (m, 4H), 2.42 (q, $J = 6.9$ Hz, 4H) was measured, as given in Supplementary Fig. 1b.



Supplementary Fig. 1 | ^1H -NMR spectrum. a, Liquid-state ^1H -NMR spectrum of compound 1,2,5,6-tetrabromocyclooctane (**1**). **b**, Liquid-state ^1H -NMR spectrum of compound 1,5-dibromo-1,5-cyclooctadiene (**2**).

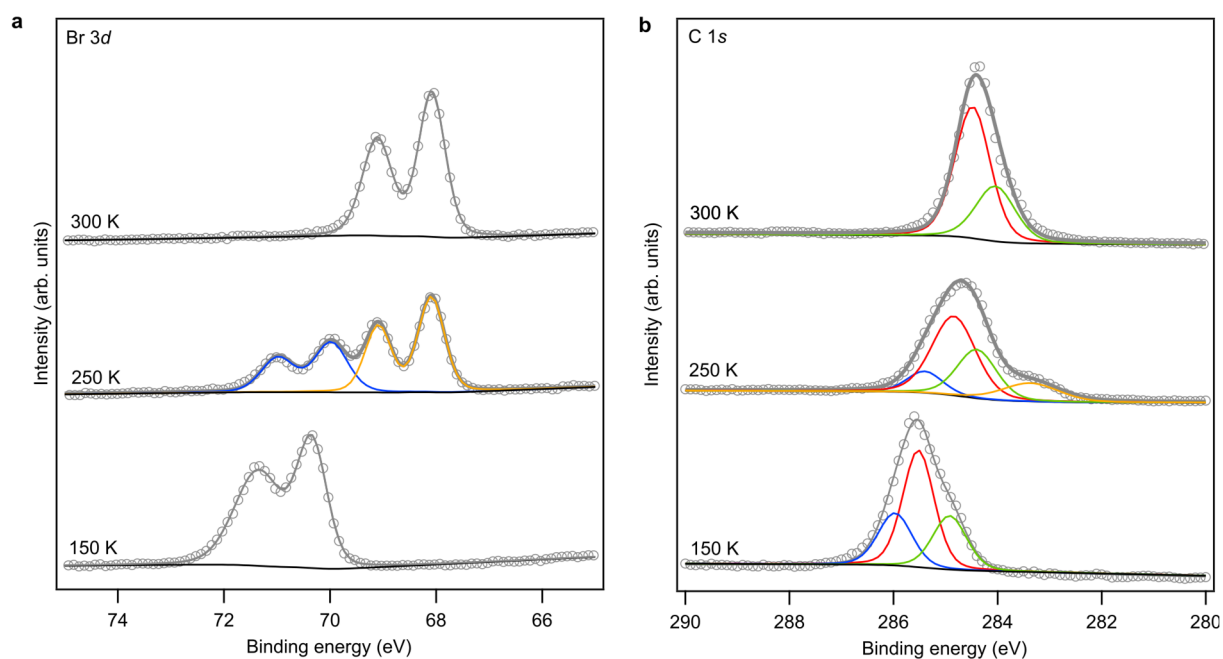
Supplementary Section 1. Deposition of DBCOD on Ag(111) prepared at 300 K



Supplementary Fig. 2 | Overview image of PCOD chains. Large-scale STM image (1.0 V and 20 pA) recorded after deposition of DBCOD onto Ag(111) at 300 K. The equivalent orientations for the PCOD chains were observed, as marked by the arrowed star.

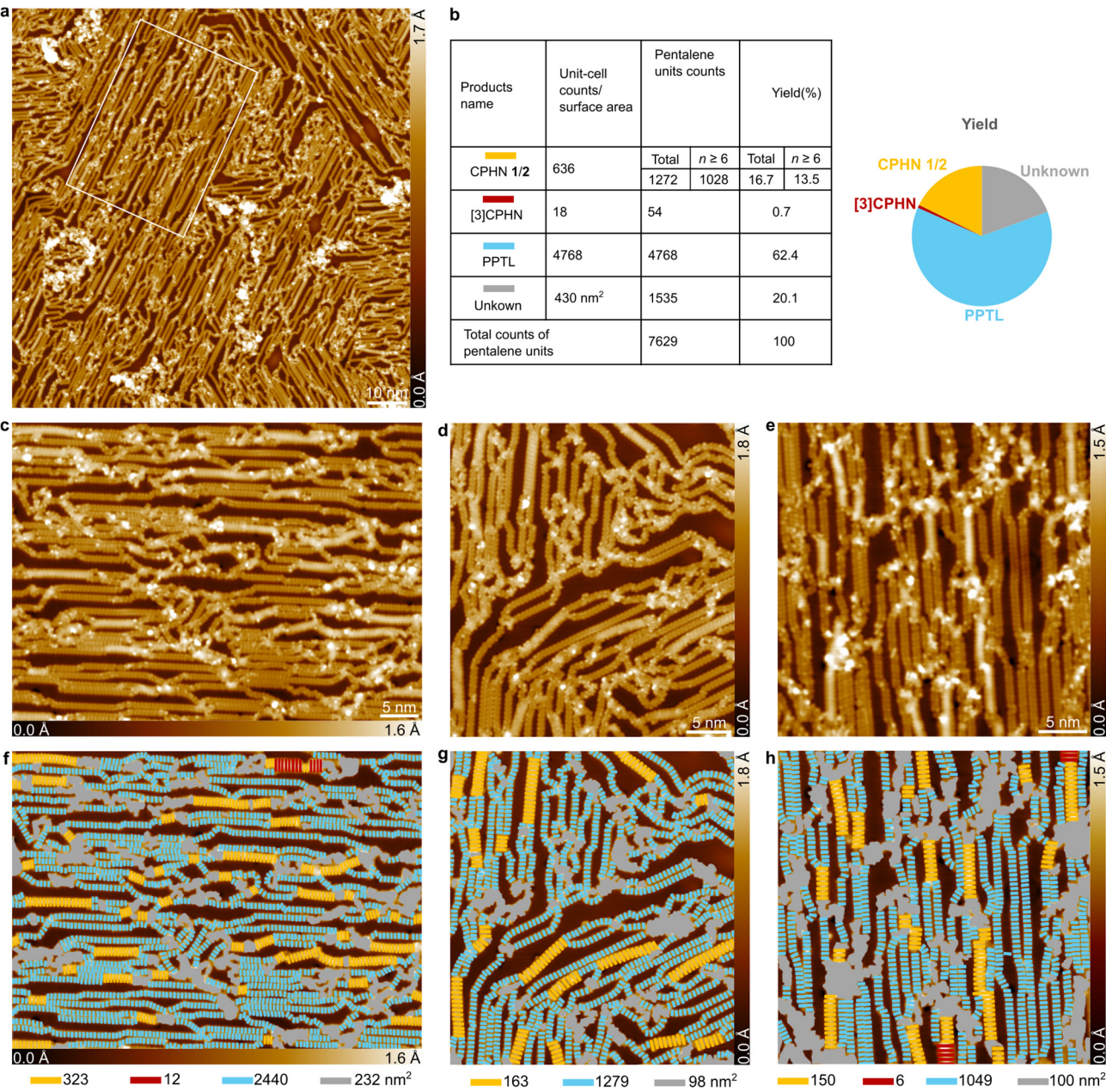
Supplementary Section 2. Room temperature C–C covalent coupling of DBCOD demonstrated by SRPES

To further confirm the C–C covalently bonded polymer phase formed by DBCOD at 300 K, we have performed SPRES by deposition of DBCOD onto Ag(111) at 150 K followed by annealing to 250 K and 300 K. As shown in Supplementary Fig. 3a, the Br 3*d* spectrum at 150 K shows a single doublet centered at binding energies (BE) of 71.2 eV (Br 3*d*_{3/2}) and 70.2 eV (Br 3*d*_{5/2}), respectively. According to the previous report², these peaks are associated with the C–Br bonds of intact DBCOD molecules. The corresponding C 1*s* spectrum at 150 K (Supplementary Fig. 3b) again supports this claim, which is deconvoluted into three components for carbon in C–Br (blue curve), *sp*³ C–H (red) and *sp*² C–H (green), in agreement with the stoichiometric ratio (1:2:1) for intact DBCOD. The lower C 1*s* BE of the *sp*² carbon than the *sp*³ carbon agrees with previous studies³. Further annealing of the sample to 250 K leads to the partial C–Br bond scission as demonstrated by the observation of newly appeared Br–Ag related doublet (yellow curve) located at BE of 68.1 eV and 69.1 eV (Supplementary Fig. 3a, Br 3*d*, at 250 K). Moreover, the appearance of a new low binding energy peak at 283.4 eV (yellow curve) for the C 1*s* spectrum at 250 K demonstrated the partial formation of organometallic species after C–Br bond scission. Subsequent annealing of the sample to 300 K leads to the disappearance of the C–Br related doublet and the increasing of Br–Ag related doublet as shown by the Br 3*d* spectra (Supplementary Fig. 3a, at 300 K), indicating the complete dissociation of C–Br bonds. The corresponding C 1*s* spectrum (Supplementary Fig. 3b, at 300 K) shows that the C–Ag related component at low binding energy disappears, strongly suggesting the formation of C–C covalently bonded species. The spectrum is deconvoluted into two components, including the *sp*³ and *sp*² carbon with a ratio of 2:1 in consistent with the formation of polycyclooctadiene chain.



Supplementary Fig. 3 | SRPES of DBCOD on Ag(111) at different temperatures. a,b, Br 3d and C 1s SRPES spectra taken after deposition of DBCOD molecules onto Ag(111) at 150 K, followed by annealing to 250 and 300 K, respectively. For the Br 3d spectrum at 250 K, the blue and yellow peaks are components related to C–Br and Ag–Br bonds. For the C 1s spectra, the blue, red, green and yellow component curves are related to the carbon in C–Br bond, sp^3 C, sp^2 C, and C–Ag bond, respectively.

Supplementary Section 3. Statistical analysis of CPHN and PPTL yields and ratios

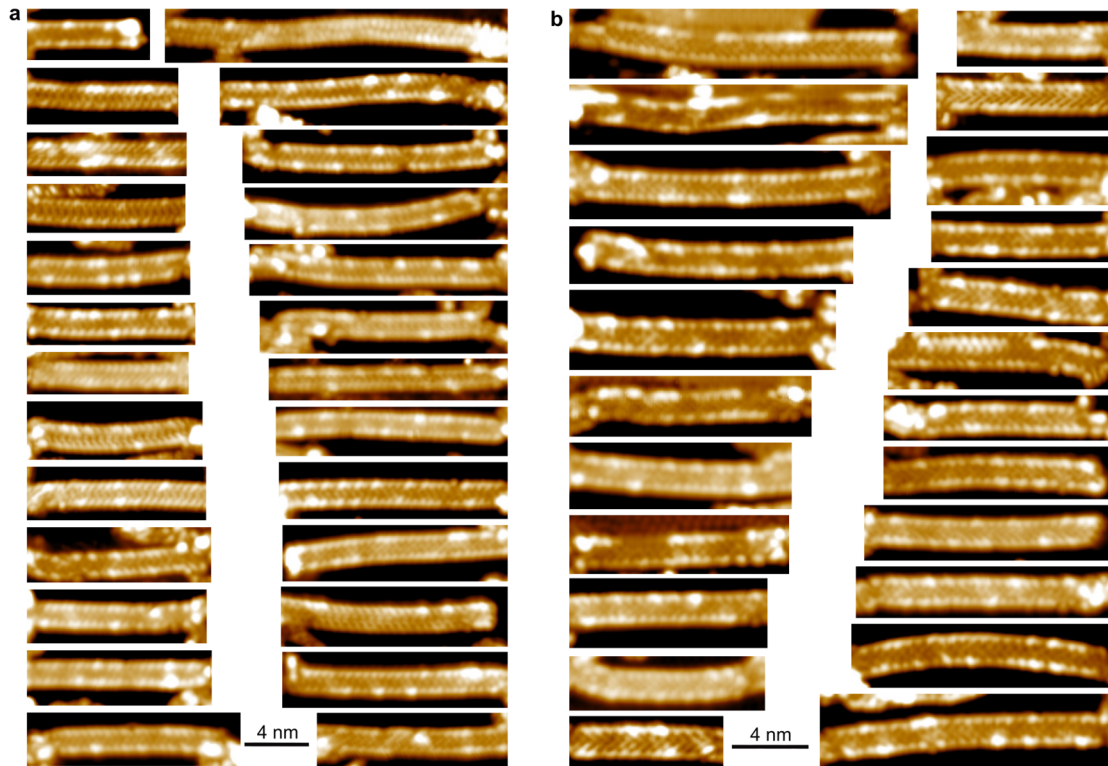


Supplementary Fig. 4 | Statistical analysis of CPHN yields. **a**, Large-area STM overview image acquired on Ag(111) after growth under optimized conditions (deposition of a full monolayer of DBCOD, followed by annealing at 773 K for 2 h after PPTL formation). **b**, Summary table of the pentalene-unit counts extracted from the STM images in **c–e**. n is the number of CPHN 1/2 repeating units in an individual segment. **c**, Magnified STM image of the region outlined in white in **a**. **d,e**, Representative STM images from two other regions of the same sample, illustrating the coexistence of CPHNs and by-products. **f–h**, Annotated versions of panels **c–e**, respectively. Yellow sticks mark repeating units of CPHN 1/2, blue sticks mark PPTL chains, red sticks mark [3]CPHN, and gray shaded regions denote unknown/disordered structures. The CPHN yield is defined as the fraction of

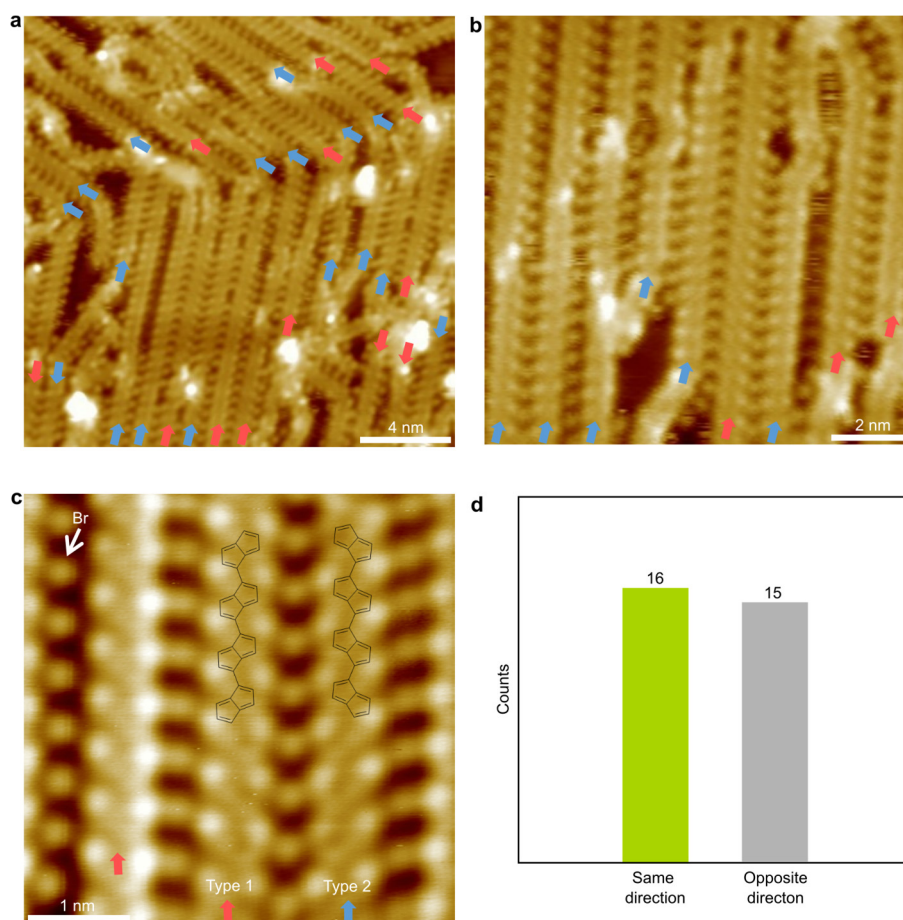
pentalene units incorporated into CPHNs:

$$\text{Yield} = (N_{\text{CPHN } 1/2} + N_{[3]\text{CPHN}}) / (N_{\text{CPHN } 1/2} + N_{[3]\text{CPHN}} + N_{\text{PPTL}} + N_{\text{Unknown}})$$

Here, $N_{\text{CPHN } 1/2}$, $N_{[3]\text{CPHN}}$, and N_{PPTL} are obtained by counting the numbers of pentalene units assigned to all CPHNs (yellow and red) and PPTL (cyan), respectively (values listed in **b**). The number of pentalene units in disordered regions, N_{Unknown} , is estimated by multiplying the gray-shaded area by the areal density of pentalene units (3.56 pentalene units per nm²). This density is determined from **g**, where 326 pentalene units occupy an area of ~92 nm² covered by CPHNs. Note that one CPHN 1/2 repeat unit (yellow stick) and one [3]CPHN repeat unit (red stick) contain two and three pentalene units, respectively. From the statistical analysis of the three images in **c–e**, the overall assigned CPHN yield is 17.4%, including 16.7% for CPHN 1/2 and 0.7% for [3]CPHN. The yield of CPHN 1/2 segments containing at least six repeating units ($n \geq 6$) is 13.5%, calculated from the corresponding pentalene-unit count. All STM images were acquired with CO-functionalized tips at $U = -1.0$ V, $I = 20$ pA.

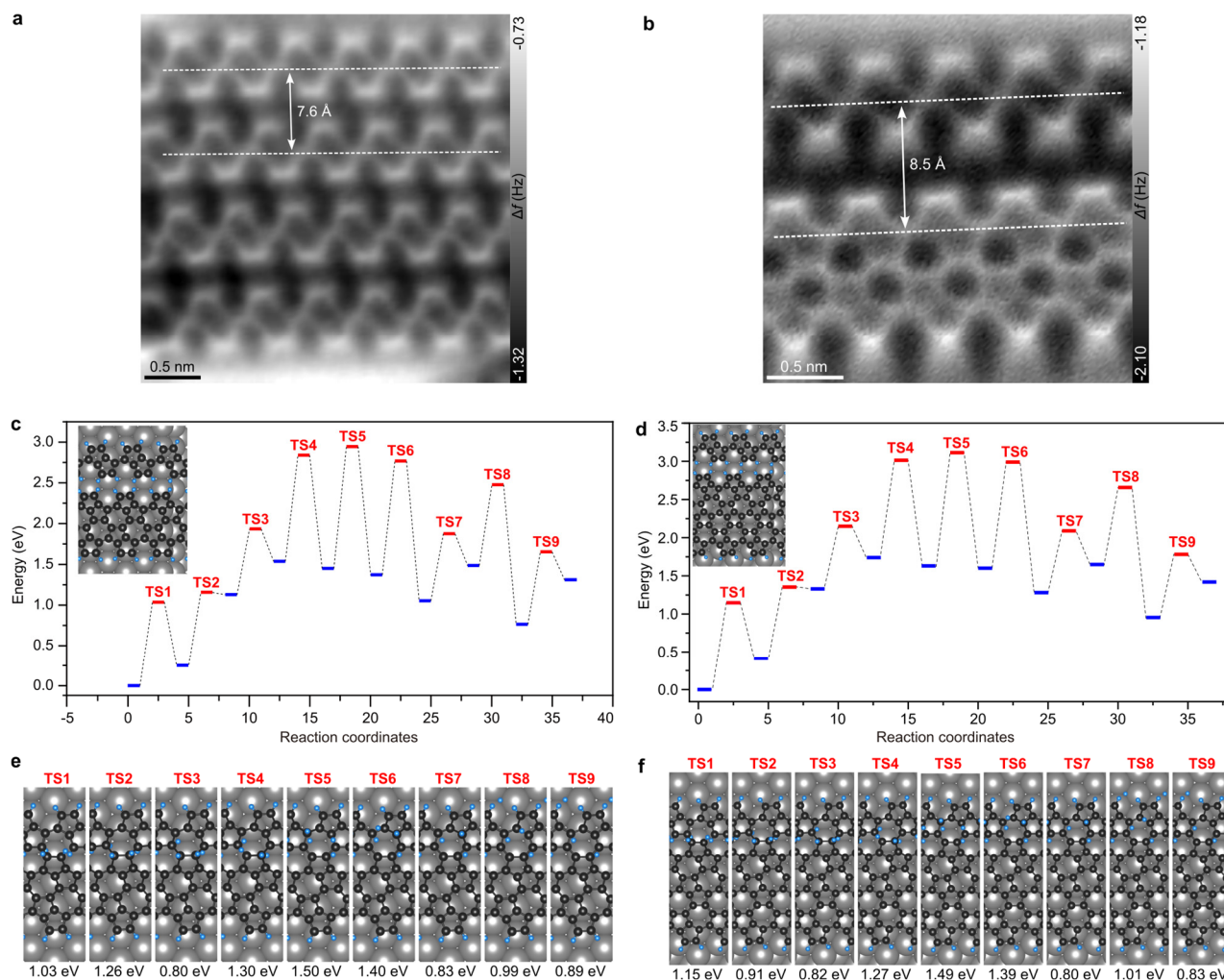


Supplementary Fig. 5 | Statistical analysis of the yield ratio between CPHN 1 and 2. **a,b,** Zoomed-in STM images of 49 randomly selected CPHNs observed in the sample with an optimized growth condition: a full monolayer DBCOD and an annealing temperature of 773 K for duration of 2 hours after PPTL formation. For clarity, 26 CPHN **1** and 23 CPHN **2** are separated into **a** and **b**, respectively, which are classified by their metallic and semiconducting behaviors based on their differential conductance (dI/dV) curves in addition to the patterns in the STM images.



Supplementary Fig. 6 | Domains of PPTL chains. **a,b**, Large scale STM images (0.1 V and 20 pA) of two different domains of PPTL chains acquired after annealing the PCOD chains to 623 K. **c**, Magnified STM (0.1 V and 20 pA) image of PPTL chains co-adsorbed with Br adatoms. The orientation of the pentalene moieties could be resolved by the lobes at the chain edges as illustrated by the superposed chemical structures. The parallelly arrayed PPTL chains are divided into type 1 and 2 according to the two different orientations of their pentalene moieties. **d**, Statistics showing the adjacent PPTL chain pairs with the same and opposite pentalene orientations. According to the marked PPTL chains of 18 in type 1 and 23 in type 2, the number of chain pairs containing uniform and different types of PPTLs are counted to be 16 and 15, respectively.

Supplementary Section 4. Additional comparison of separations between PPTLs and between a PPTL and a formed CPHN, and calculated reaction pathways for forming [3]CPHNs



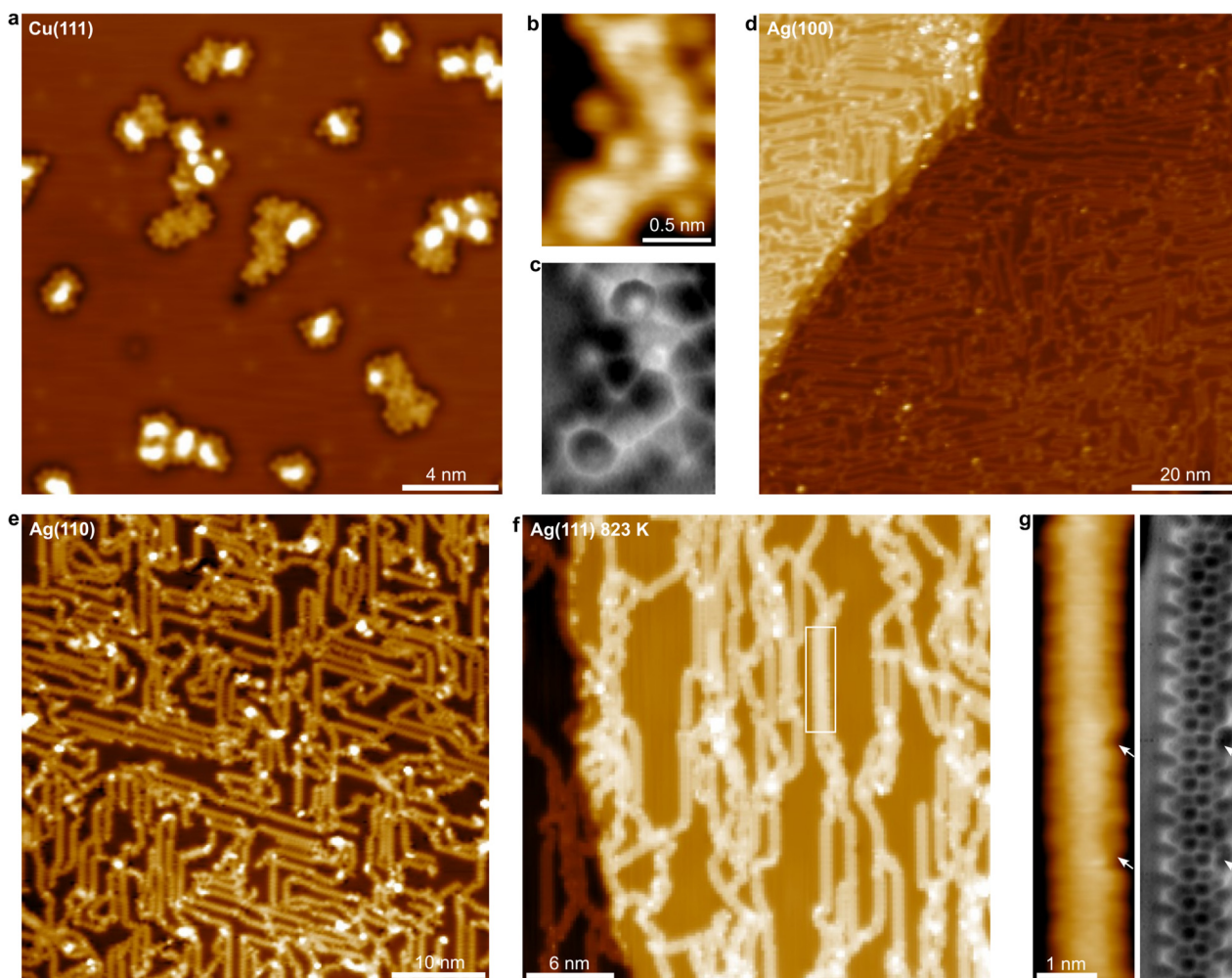
Supplementary Fig. 7 | Calculated reaction pathways for the fusion between PPTL and CPHN

1. a,b, nc-AFM images (identical to Fig. 1i and Extended Data Fig. 2j) showing the distances of PPTL-PPTL and PPTL-CPHN **1**. **c,d**, CI-NEB simulations for the reaction pathway of the lateral fusion of the aligned PPTL with CPHN **1** in **c** and with [3]CPHN in **d** for the formation of wider CPHNs. The insets show the structural models of the initial states. **e,f**, The structures of the transition state in **c** and **d**, respectively. The highest activation barriers for the fusion of PPTL with CPHN **1** and [3]CPHN are 1.50 and 1.49 eV, respectively.

Supplementary Section 5. Optimization of the synthesis of CPHNs by using different coinage surfaces and annealing temperatures

In addition to Ag(111), we investigated several other coinage metal surfaces for the on-surface synthesis of CPHNs from the DBCOD precursor monomer, including Cu(111), Ag(100), Ag(110), Au(111), Au(110), and Au(100). Due to the relatively low molecular weight of the DBCOD monomer, it readily desorbs from all examined gold surfaces prior to thermal activation necessary for Ullmann coupling. On Cu(111), deposition of DBCOD at 300 K did not result in the formation of PCOD chains. Subsequent annealing to 400 K led to the formation of short C–C coupled oligomers (Supplementary Fig. 8a); however, significant ring opening of some cyclooctadiene (COD) units was observed, as evidenced in Supplementary Fig. 8b,c. In contrast, the other two silver facets were found to be favorable for the synthesis of PPTL chains. As shown in Supplementary Fig. 8d,e, reactions of DBCOD on both Ag(100) and Ag(110) successfully produced PPTL chains. Nevertheless, compared to Ag(111), the reduced surface mobility of these chains on Ag(100) and Ag(110) appears to hinder their lateral fusion into extended CPHN structures. Among all tested substrates, Ag(111) remains the most effective surface for the on-surface synthesis of CPHNs.

Regarding the Ag(111) surface, the attempts of increasing the yield and width of CPHNs by annealing to higher temperature (823 K) for extended durations (Supplementary Fig. 8f) lead to decomposition of the CPHN structures by destroying the rings at the edges as shown by the magnified STM and nc-AFM images in Supplementary Fig. 8g (white arrows). This occurs because once the sample reaches a temperature sufficient to cleave the C–C bond linking the CPHN to the PPTL chain, the internal C–C bonds within the pentagons and heptagons tend to be destabilized and destroyed. Therefore, the optimization of the yields of CPHN **1** and **2** is possible by annealing of a full monolayer DBCOD at temperature of 773 K for long duration of 2 hours after PPTL formation (Supplementary Fig. 4). However, the yields are still limited owing to the lowered mobility of the covalent tethered PPTLs during the lateral fusion reaction.



Supplementary Fig. 8 | Attempts to optimize the synthesis of CPHNs using different surfaces and annealing temperatures. **a**, STM image taken after deposition of DBCOD onto Cu(111) held at 300 K followed by annealing to 400 K. **b,c**, Zoom-in STM and nc-AFM images of the typical products formed in **a**. **d,e**, Large-scale STM images taken after deposition of DBCOD onto Ag(100) and Ag(110) surfaces at 300 K followed by annealing to 623 K. **f**, Large-scale STM image taken after annealing of the CPHNs sample to 823 K. **g**, Zoom-in STM and nc-AFM images of the white framed region in **f**. Tunneling parameters for the STM images in **a–d**: **a**, 1.0 V, 20 pA; **b**, 1.0 V, 50 pA; **d**, –0.5 V, 50 pA; **e**, –0.1 V, 50 pA; **f,g**, –0.1 V, 20 pA; The nc-AFM image in **c** and **g** is recorded using constant-height mode at a tip height of –50 and –40 pm with respect to the height at the STM setpoint of –10 mV, 20 pA over the adsorbates.

Supplementary Section 6. The details of lifting process for the transport measurements and additional data

Prior to conducting the lifting experiments, the STM tip was routinely conditioned through multiple cycles to ensure a stable and robust tip–ribbon contact. To establish a strong mechanical and electronic connection between the tip and the CPHN molecule (ideally involving multiple carbon atoms binding to the tip), the tip was advanced toward the ribbon until a sudden current jump was detected, indicating contact formation (blue, green and red arrows in Extended Data Fig. 4d,e). To further reinforce the tip–CPHN interaction, the tip was subsequently moved an additional 0.1~0.2 nm beyond this initial contact point before commencing the retraction along the lifting trajectory shown in Extended Data Fig. 4d.

To mitigate the influence of variations in terminal structures and tip–ribbon contact on the measured conductance, lifting experiments were performed on three CPHN **1** and two CPHN **2** samples (Supplementary Fig. 9a,b). As demonstrated in Supplementary Fig. 9a, fluctuations in contact geometry and terminal structure can influence contact resistance, thereby affecting the absolute value of the transport conductance. Nevertheless, the overall conductance magnitude and decay constant (β) remained largely consistent across different samples. For instance, the stable lifting trace for CPHN **1** (sample #2) shows an average conductance of approximately $0.5G_0$, slightly lower than the $\sim 0.9G_0$ observed in CPHN **1** (sample #1) discussed in the main text. Despite these variations, the decay constant β exhibited minimal change, indicating negligible conductance decay within the 1–3 nm range under different lifting biases.

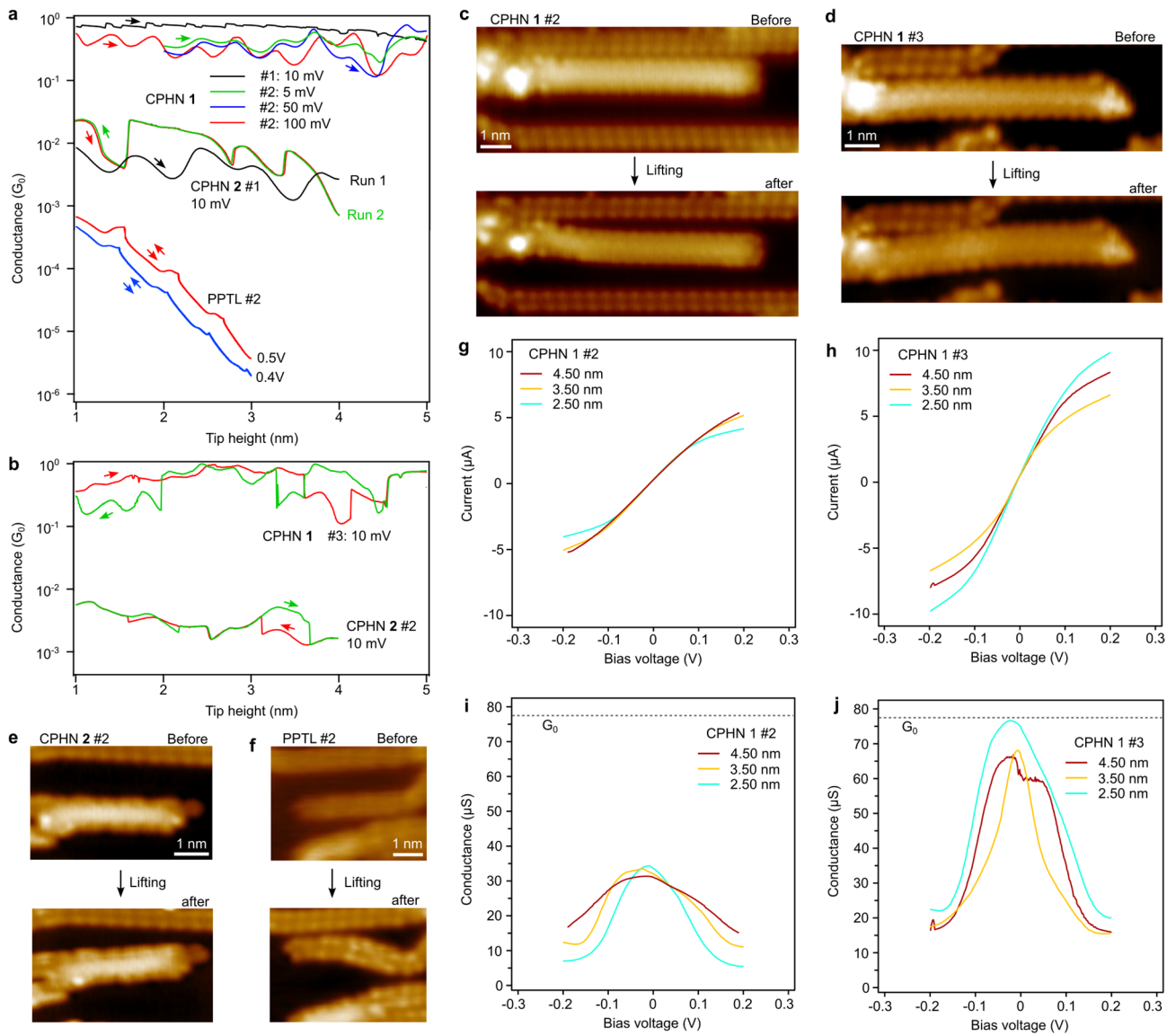
This behavior is consistent with the expected characteristics of resonant transport in metallic systems. In this regime, the Fermi level of the electrodes aligns with the molecular energy levels, enabling ballistic electron transport through the molecule. As a result, the conductance is primarily governed by the contact resistance, which depends on the coupling strength between the molecular orbitals and the electrodes⁴. Consequently, although the absolute conductance may vary with changes in the tip–molecule contact, the decay constant β remains essentially unaffected. This switching of contact resistance due to tip–ribbon interface variability is directly evidenced by the lifting experiment on CPHN **1** (sample #3), where a clear conductance jump between $\sim 0.3G_0$ to $\sim 0.8G_0$ was observed during a bidirectional (upward and downward) tip movement (upper red and green curves,

Supplementary Fig. 9b). A similar conductance jump was also recorded for CPHN **2** (sample #2), as shown by the bottom red and green curves in Supplementary Fig. 9b.

Beyond contact-geometry variations, the accessible bias window for STM-lifting transport on CPHN **1** is also limited by the intrinsically high conductance of the contacted junction, which rapidly drives the current into the μA regime with the increase of bias voltage. In our measurements, the current already approaches (and can exceed) $10\text{ }\mu\text{A}$ at biases of $\pm 0.2\text{ V}$, which is near the practical operating limit of our STM-based transport setup. While conventional STM feedback and imaging are typically optimized for the nA range ($\leq 10\text{ nA}$), operation in the μA range requires a substantially reduced transimpedance gain, leading to reduced current sensitivity and making stable feedback control and simultaneous high-quality imaging more challenging. Consequently, the bias range of -0.2 to $+0.2\text{ V}$ used in the main text represents the widest window that could be obtained reproducibly after repeated attempts while maintaining a stable junction.

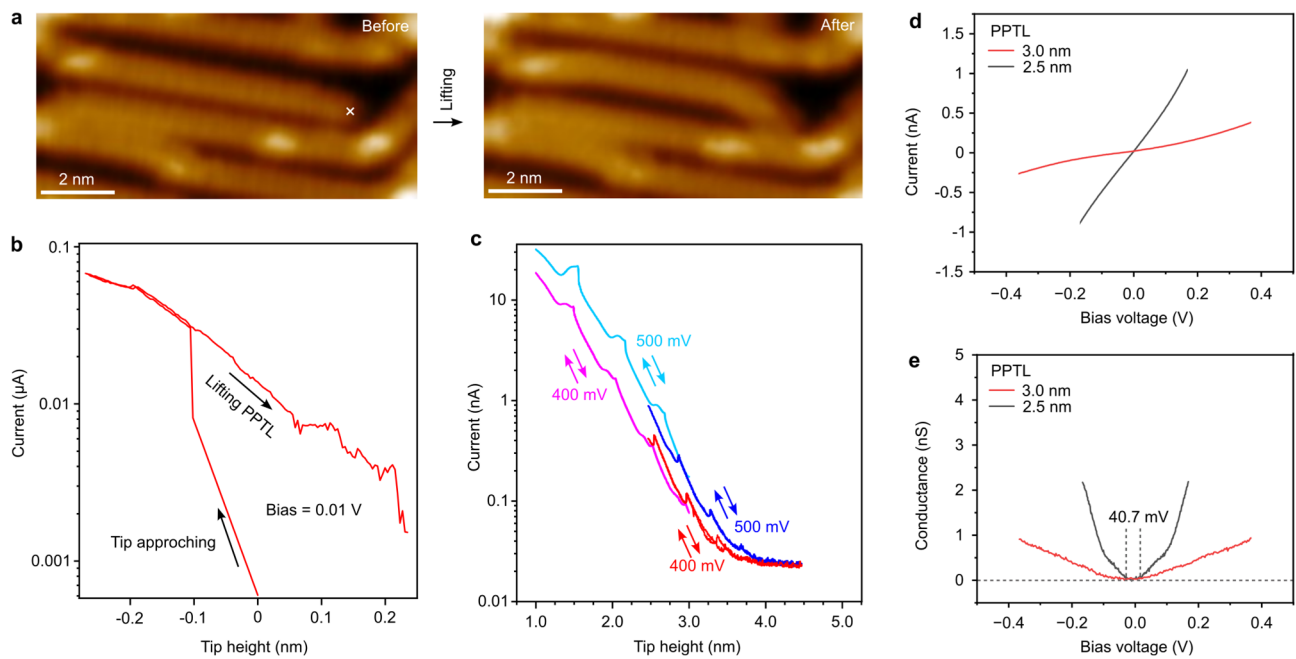
Importantly, the combination of high conductance and finite bias increases Joule heating in the lifted CPHN **1** junction, which can irreversibly damage the ribbon during an I - V sweep. This limitation is illustrated in Supplementary Fig. 13: the intact CPHN **1** ribbon (Supplementary Fig. 13a) becomes irreversibly damaged after a subsequent high-current I - V sweep as marked by the magenta arrow in Supplementary Fig. 13e. Notably, a sudden reduction in the I - V (Supplementary Fig. 13c) and dI/dV (Supplementary Fig. 13d) signal occurs when the current reaches $\sim 2.5\text{ }\mu\text{A}$. We note that junction failure during extended I - V sweeps was common for CPHN **1**, and many ribbons did not survive the full sweep once the current entered the several- μA range. Therefore, substantially wider bias sweeps are technically not feasible within the intrinsic constraints of STM-lifting transport for this highly conducting system. Nevertheless, within the accessible bias window, the reproducible near-zero-bias conductance enhancement, together with our contact-geometry calculations, supports a plausible contact-induced near- E_F level-alignment scenario rather than a unique proof of strict Fermi-level pinning.

Finally, a possible existing Kondo resonance (due to the defect-induced magnetic moment) from a lifted end can be largely excluded, since the ends of manipulated CPHN **1** did not show Kondo resonance when they sit on the Ag(111) surface (Supplementary Fig. 11).

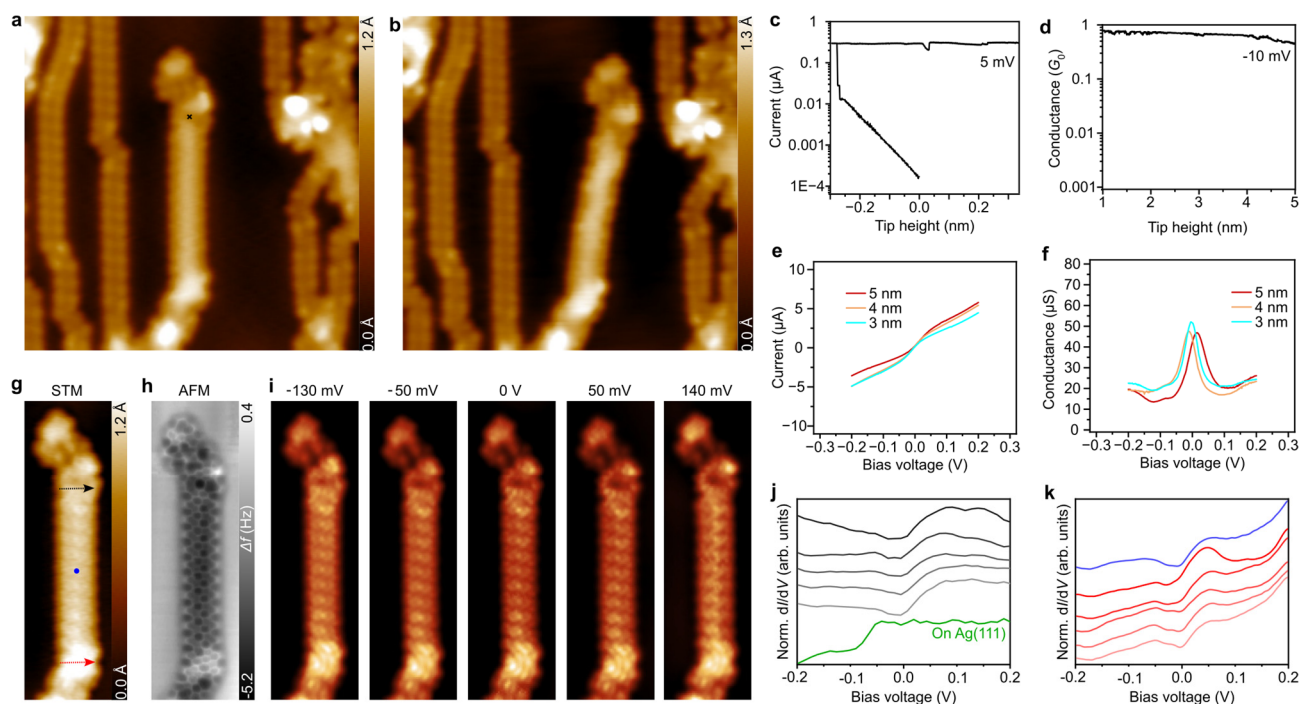


Supplementary Fig. 9 | Transport measurements of additional CPHNs. **a**, Conductance (in units of G_0) as a function of tip height for different lifting experiments involving two CPHN 1, two CPHN 2, and one PPTL. The number #1 ribbons of CPHNs 1, 2 and PPTL are shown in the main text, while additional CPHNs and PPTL are presented in **c–f**. The applied bias during continuous tip lifting is indicated. The arrows near the conductance curves indicate the moving directions of the tip (downwards or upwards). For PPTL, the paired arrows at each bias voltage indicate that the upward and downward traces almost completely overlap. Two independent lifting experiments on the same CPHN 2 (run 1 and run 2) are shown, each exhibiting a distinct tip–ribbon contact. **b**, Conductance (in units of G_0) as a function of tip height for the lifting of CPHN 1 #3 and CPHN 2 #2, showing a reversal in the tip’s up-and-down trace. Several conductance jumps are observed, attributed to changes in the tip–ribbon contact. **c–f**, STM images (–0.1 V, 10 nA) taken before and after the lifting experiments for CPHN 1 #2 (**c**), CPHN 1 #3 (**d**), CPHN 2 #2 (**e**), and PPTL #2 (**f**) as labeled. **g,h**, I – V

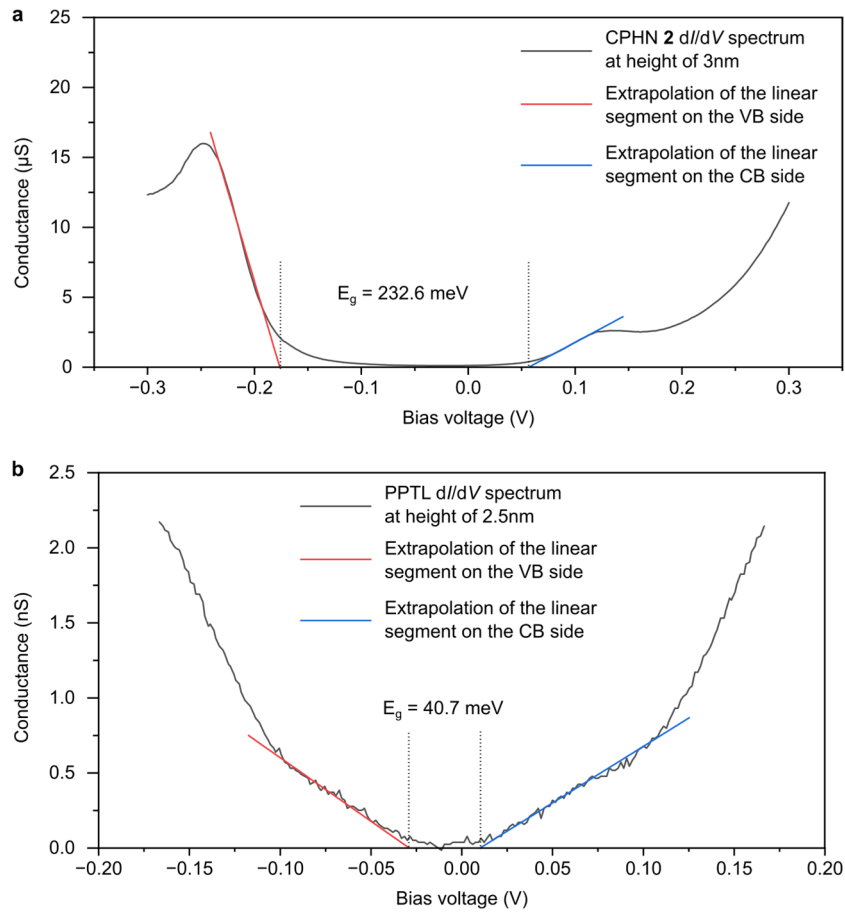
curves measured at the indicated retraction heights for CPHNs **1** #2 and #3, respectively. **i,j**, Numerically derived dI/dV spectra of CPHNs **1** #2 and #3 from the $I-V$ curves in **g,h**, respectively. Note that these numerically derived dI/dV spectra may not be used to directly compare with the single-site dI/dV spectra measured at tunnelling mode.



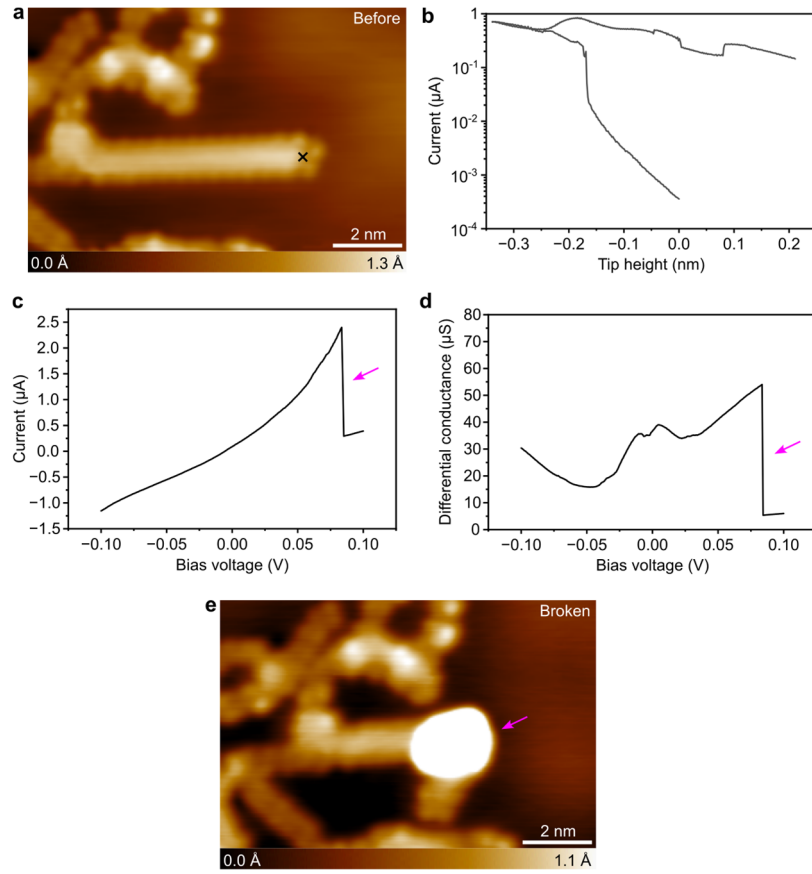
Supplementary Fig. 10 | Lifting experiments of PPTL. **a**, STM image of PPTL with one terminal taken before and after the lifting experiments. Setpoint conditions: -0.1 V and 10 nA. The white cross marked out the initial tip position in the xy plane during the lifting process. **b**, Plot of the current (logarithmic scale) versus relative tip height for the lifting of PPTL on Ag(111), showing the sudden change in the conductance once the ribbon has been contacted with the STM tip. The zero value of the relative tip height is set to the STM setpoint of -0.1 V and 10 nA. The bias during the lifting experiments is 0.01 V. **c**, Logarithmic plot of current versus relative tip height during the lifting of PPTL (including reversal traces). Curves correspond to lifting from 1 – 3 nm (cyan and pink) and 2.5 – 4.5 nm (blue and red) at applied biases of 400 mV and 500 mV, as indicated. The arrows near the conductance curves indicate the moving directions of the tip (downwards or upwards). The paired conductance curves in cyan and magenta at each bias voltage almost completely overlap. The blue and red conductance curves represent paired measurements from separate experimental runs on the same PPTL at extended lifting heights. This approach prevents complete data loss that could occur if the PPTL drops during extended lifting. **d,e**, I – V and dI/dV curves measured at the indicated retraction heights for PPTL. The details of the transport-gap definition are shown in Supplementary Fig. 12.



Supplementary Fig. 11 | Transport and spectroscopic measurements on the same single-terminated CPHN 1 ribbon. **a,b**, Overview STM images of a single-terminated CPHN 1 ribbon on Ag(111) before (**a**) and after (**b**) tip-lifting manipulation for transport measurements. **c**, Current (log scale) as a function of relative tip height during lifting at the position marked by the black cross in **a**, showing an abrupt conductance change upon establishing contact between the STM tip and the ribbon. The relative height $z = 0$ is defined at the STM setpoint ($U = -0.1$ V, $I = 1$ nA); the lifting bias is 5 mV. **d**, Conductance (in units of G_0) versus tip height (1–5 nm) for the lifted CPHN 1 junction. **e,f**, I - V and dI/dV characteristics measured at the indicated retraction heights during the transport experiment. **g–i**, Zoomed-in STM (**g**), nc-AFM (**h**), and dI/dV maps (**i**) of the same ribbon (region indicated in **a**) acquired with a CO-functionalized tip. The dI/dV maps in **i** were recorded at the bias voltages labeled in the panel. **j,k**, Normalized stacked dI/dV spectra acquired at the top and bottom terminal sites, as indicated by the black and red arrows in **g**, respectively. The green trace in **j** was recorded on Ag(111) for reference. The blue trace in **k** was acquired at the ribbon center (blue dot in **g**). Spectra are plotted from bottom to top and vertically offset for clarity. Imaging/measurement parameters: **a,b**, $U = -0.1$ V, $I = 1$ nA; **g**, $U = -0.1$ V, $I = 50$ pA; **h**, z -offset = 0 pm relative to the STM setpoint ($U = -5$ mV, $I = 50$ pA).



Supplementary Fig. 12 | Transport-gap extraction by linear extrapolation (line-intersection method). **a,b**, Linear-extrapolation analysis of the transport $dI/dV(V)$ spectra of CPHN **2** (**a**) and PPTL (**b**), using the same datasets as in Fig. 2i (CPHN **2**, 3 nm) and Supplementary Fig. 10e (2.5 nm), respectively. The transport gap is defined as $E_g = e(V_+ - V_-)$, where V_- and V_+ are the onset biases on the occupied (VB) and unoccupied (CB) sides, respectively (vertical dashed lines). The VB and CB onsets are obtained by fitting straight lines to the quasi-linear leading-edge segments of the first VB/CB features closest to E_F (red and blue) and defining V_- and V_+ as the intersection points of these leading-edge fits with the low-conductance background (baseline; black dashed line).

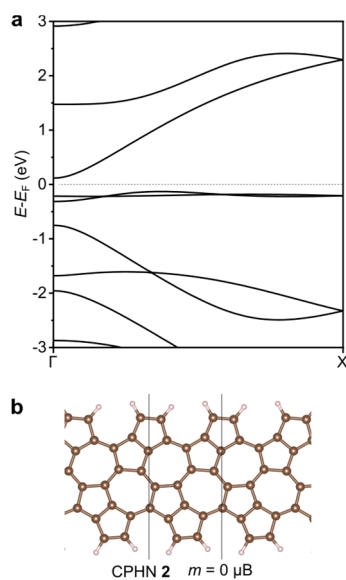


Supplementary Fig. 13 | Irreversible damage of a CPHN 1 ribbon during an I – V sweep in the transport experiment. **a,e**, STM images of the same area (-0.1 V, 10 nA) showing the ribbon before manipulation (**a**), and after damage induced by a high-current I – V sweep (**e**). **b**, Current (log scale) as a function of relative tip height during lifting at the position marked by the black cross in **a**, revealing an abrupt conductance change upon establishing contact between the STM tip and the ribbon. The relative height $z = 0$ is defined at the STM setpoint ($U = -0.1$ V, $I = 1$ nA); the lifting bias is 5 mV. **c,d**, I – V (**c**) and dI/dV (**d**) spectra acquired at a tip retraction of 3 nm during the transport measurement, showing a sudden reduction (marked by magenta arrow) in signal when the current reaches ~ 2.5 μ A. This abrupt change is attributed to irreversible damage of the CPHN **1** ribbon, as indicated by the magenta arrow in panel **e**.

Supplementary Section 7. Negligible magnetism both in CPHN 1 and 2

To further judge the possibly existing magnetic property, the band structures of CPHN 1 and 2 are also calculated using spin-polarized DFT (Extended Data Fig. 5). The spin-splitting in the band structure of freestanding CPHN 1 is observed with employing PBE and HSE06 functionals (Extended Data Fig. 5a,b), which give similar net magnetic moment of around $0.4 \mu_B$ per repeating unit (Extended Data Fig. 5f,g). In contrast, no spin-splitting is observed for CPHN 1 on Ag(111) (Extended Data Fig. 5c), showing the band structure similar to the one using spin-unpolarized DFT (Extended Data Fig. 6b). The magnetism of freestanding CPHN 1 can be attributed to the flat-band ferromagnetism due to the strong on-site coulomb repulsion of the spatially localized electrons (in the nearly flat metallic band) at the E_F . The corresponding spin density distributions (Extended Data Fig. 5f,g) show that the spin-polarized states are not confined to the ribbon edges but are instead delocalized across the entire ribbon. However, this magnetism is quite fragile and highly sensitive to doping. As observed in Extended Data Fig. 5e,j, a slight doping of 0.1 electron per unit cell can lead to the absence of spin splitting.

For CPHN 2, no spin splitting is observed in the band structure obtained using spin-polarized DFT (Supplementary Fig. 14), similar to the results obtained using spin-unpolarized. This absence of magnetism can be rationalized by examining the electronic structure: the magnetism in CPHN 1 originates from strong on-site Coulomb repulsion among spatially localized electrons residing in a nearly flat metallic band at the Fermi level. For CPHN 2, however, this flat band is shifted below the Fermi energy due to its semiconducting nature, thereby eliminating the conditions necessary for spin splitting.



Supplementary Fig. 14 | Calculated band structures of CPHN 2 with spin polarization. a, DFT-calculated band structures of freestanding CPHN 2 incorporating spin polarization. **b**, DFT-optimized chemical structures of freestanding CPHN 2 using GGA-PBE functional.

Supplementary Section 8. Details of the SSH ladder tight-binding model for PPTL and CPHNs

To gain insight into the band structures of PPTL, CPHN **1** and **2**, we adopt an extended Su–Schrieffer–Heeger (SSH) model using Hamiltonian:

$$H_{\text{PPTL}} = \sum_i \varepsilon_i \alpha_i^\dagger \alpha_i + \sum_n \sum_{i \neq j} t(i_n, j_n) \alpha_{n,i}^\dagger \alpha_{n,j} + \sum_n \sum_{i,j} t(i_n, j_{n+1}) \alpha_{n,i}^\dagger \alpha_{n+1,j} + \text{H.c.}$$

for PPTL (Fig. 3a in the main text), where the index n labels the unit cell, ε_i denotes the on-site energy, and $\alpha_{n,i}$ ($\alpha_{n,i}^\dagger$) is the annihilation (creation) operator for electrons at the $i \in \{a, b, c\}$ site in the n th unit cell. Here, we consider three lattice sites per repeating unit to describe the three near- E_F bands of planar PPTL with inclusion of the nearest neighbor intracell hopping $t(i_n, j_n)$ with $i \neq j$, the nearest neighbor intercell hopping $t(c_n, a_{n+1})$, and the next-nearest neighbor intercell hopping $t(i_n, j_{n+1})$ except the term $t(c_n, a_{n+1})$ (Supplementary Fig. 15e). To describe the six near- E_F bands of CPHN **1** (Fig. 3b) and CPHN **2** (Fig. 3c), the inter-chain coupling is included in an extended SSH ladder model using Hamiltonian:

$$H_{\text{inter-chain}} = \sum_n \sum_{i,i'} t(i_n, i'_n) \alpha_{n,i}^\dagger \alpha_{n,i'} + \sum_n \sum_{i,i'} t(i_n, i'_{n+1}) \alpha_{n,i}^\dagger \alpha_{n+1,i'} + \text{H.c.},$$

where $t(i, i')$ with $i \in \{a, b, c\}$ and $i' \in \{a', b', c'\}$ is the hopping between the sites of two neighboring PPTLs (Fig. 3h,i).

Construction and parametrization of the effective SSH model. We first identify the π bands relevant to PPTL and CPHNs by orbital-projected DFT calculations and select the three near- E_F bands of an isolated planar PPTL chain as the fitting target (Supplementary Fig. 15a). The projected-weight distribution suggests three effective sites per pentylene repeat unit, motivating a minimal three-site SSH description. Accordingly, we define three effective lattice sites (Wannier centers) per pentylene unit (Supplementary Fig. 15d,e). For the coupled systems (CPHN **1** and CPHN **2**), the effective Wannier-center patterns are not obtained by a trivial duplication of those of an isolated PPTL chain. Inter-chain coupling hybridizes the low-energy π subspace and redistributes its real-space weight, which can shift the effective centers. Because CPHN **1** and CPHN **2** have different inter-chain symmetries, their dominant inter-chain hopping pathways (e.g., $t(b'_n, b_{n+1})$) and related terms

specified in the model figures) differ, leading to distinct Wannier-center arrangements for PPTL, CPHN 1, and CPHN 2. The arrangements of effective Wannier-center patterns self-consistently maintain the corresponding symmetries of $P2/m$ and $Pmc2_1$ in CPHN 1 and CPHN 2, respectively. To guide the choice of hopping processes and obtain physically reasonable initial estimates, we use Wannier90 only as an auxiliary tool: three trial projection centers are placed near the above effective sites and iteratively adjusted (together with the disentanglement/energy windows) until the Wannier-interpolated dispersion reproduces the DFT bands in the energy range of interest. From the resulting Wannier Hamiltonian, we extract the dominant hopping amplitudes, truncate long-range terms, and then refine the remaining nearest-neighbor/next-nearest-neighbor parameters by directly diagonalizing the analytic SSH Hamiltonian to best match the target DFT E - k relation. In this effective description, the “sites/orbitals” are model basis functions constrained by reproducing the low-energy dispersion with a compact parameter set. For CPHN 1 and 2, the model is extended to a 6×6 SSH ladder Hamiltonian by coupling two 3×3 PPTL blocks and fitting the relevant inter-chain hopping terms following the same strategy.

We next detail the orbital-character analysis and the stepwise inclusion of dominant hopping terms. Our calculations show that the planar structure of freestanding PPTL is globally stable relative to nonplanar structures. Projected orbital analysis indicates that the two dispersive bands at the upper and lower energy regions primarily originate from the red-colored carbon atoms (Supplementary Fig. 15b), whereas the nearly flat band is mainly localized on the two central carbon atoms (green-colored) within the pentalene unit (Supplementary Fig. 15c). Based on this projected-weight distribution, we defined three effective lattice sites (Wannier centers) per pentalene unit (Supplementary Fig. 15d,e): two at the edges (red and cyan dots), accounting for the dispersive bands, and one at the center (green dot), responsible for the flat band. The resulting SSH model for PPTL thus consists of three lattice sites per unit cell and reproduces three bands.

As shown in Supplementary Fig. 15g, incorporating the dominant hopping parameters between Wannier centers, namely, nearest-neighbor intercell $t(c_n, a_{n+1})$ and intracell $t(a_n, b_n)$, $t(a_n, c_n)$, and $t(b_n, c_n)$, yields a band structure that similar to the DFT results (Supplementary Fig. 15a). Further refinement of the band dispersion is achieved by including next-nearest neighbor intercell hopping terms $t(b_n, a_{n+1})$, $t(c_n, b_{n+1})$, and $t(c_n, c_{n+1})$, as illustrated in Supplementary Fig. 15f. This extended

SSH model accurately captures the electronic structure of the PPTL chain. In particular, the emergence of a nearly flat band is primarily attributed to the small values of the intracell hopping parameters $t(a_n, b_n)$ and $t(b_n, c_n)$.

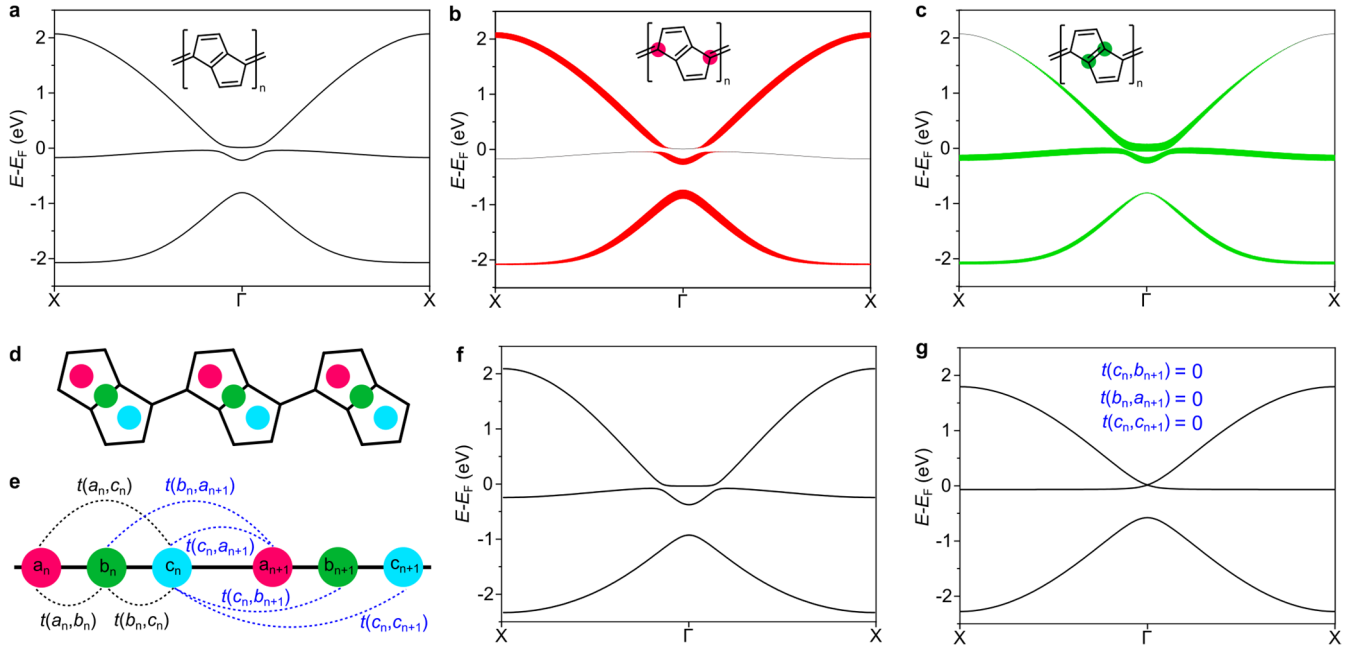
Then, the CPHN **1** and **2** could be reckoned as the SSH ladder comprising two coupled SSH chains. The difference between the coupling of the two PPTL chains leads to their different electronic behaviors as discussed below. Supplementary Fig. 16a,b shows the SSH ladder model of CPHN **1** with eight dominant inter-chain hopping parameters displayed. In the n th unit cell, the upper and lower PPTL chains are indexed in sequence of a–b–c and c'–b'–a' from left to right, respectively, highlighting the inversion symmetry of CPHN **1**. Under these parameters, the derived six bands of CPHN **1** given by the SSH ladder model (Supplementary Fig. 16f) agrees well with the DFT-calculated band structures (Fig. 3e, red solid curves). Note that the intra-chain hopping parameters (detailed in figure captions) of PPTL components in CPHN **1** are slightly different from that in the independent PPTL chain owing to the inter-chain coupling.

In order to elucidate the role of inter-chain hopping, the hypothetical band structure (Supplementary Fig. 16c) given by the SSH ladder model without inter-chain hopping is given for comparison. This band structure contains two sets of degenerated bands; each set has three bands resembling the band structure of isolated PPTL given by the SSH model. Therefore, the inter-chain coupling leads to the splitting of these two sets of bands. Thus, the metallicity of CPHN **1** originates from the overlap between the cyan band and red band.

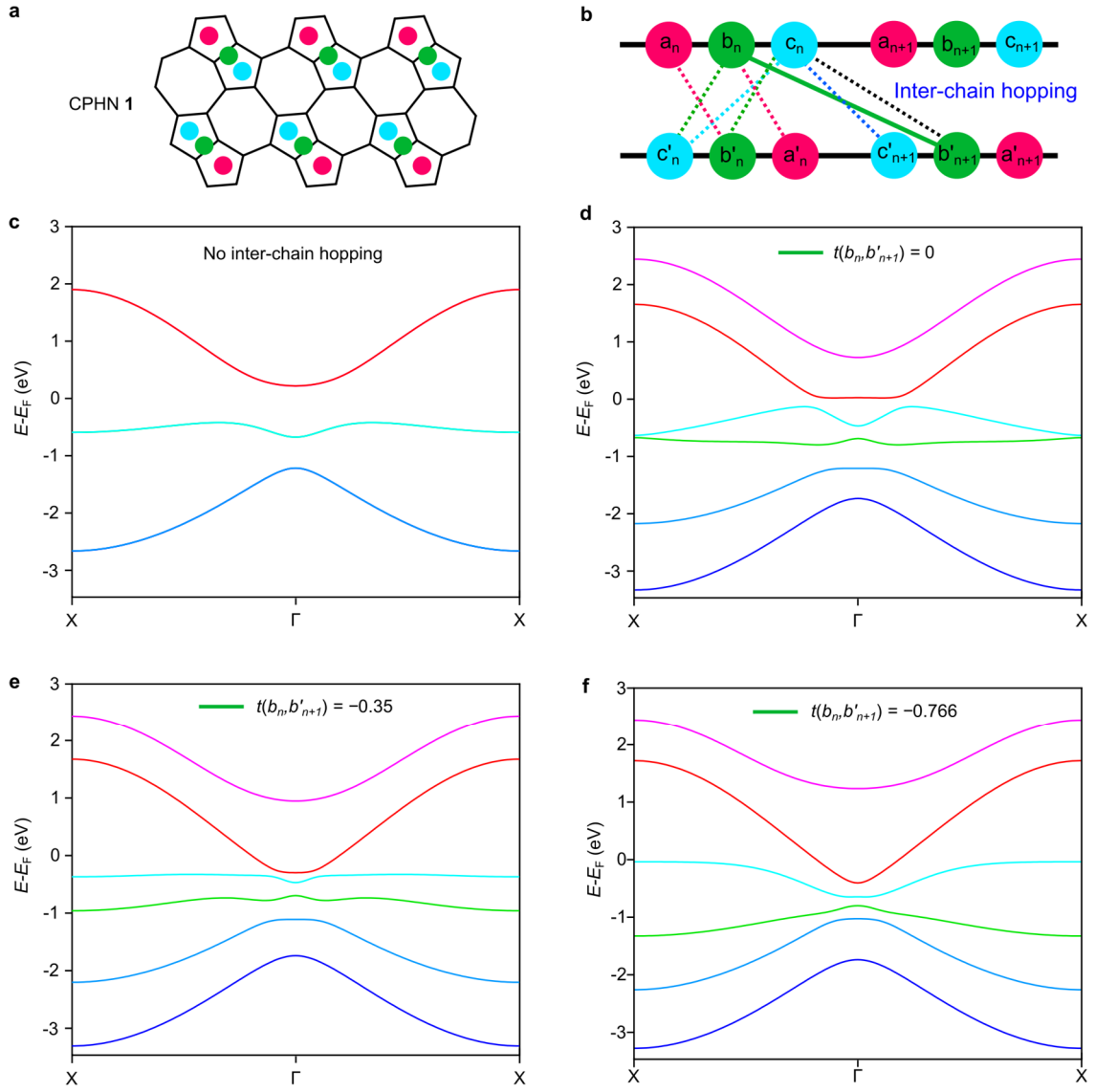
The overlap between the cyan and red bands is primarily governed by the dispersion of the cyan band. As the cyan band becomes more upward-dispersing, it increasingly overlaps with the red band. As discussed above, the cyan band originates from the nearly flat band of the isolated PPTL chain. Enhancing its dispersion requires strong inter-chain coupling. Since the flat band in PPTL is mainly localized on the central Wannier center (green dots in Supplementary Fig. 16b), a significant coupling between these central sites is necessary to induce appreciable dispersion in the cyan band. In our SSH ladder model for CPHN **1** (Supplementary Fig. 16b), this coupling corresponds to the inter-chain hopping amplitude $t(b'_n, b_{n+1})$, which connects the two green sites from the upper and lower chains, as indicated by the green solid line. When $t(b'_n, b_{n+1})$ is set to zero, the cyan and green bands (both derived from the flat band) closely approaching each other at the X point of the Brillouin zone, and

no overlap with the red band occurs. As $t(b'_n, b_{n+1})$ increases in magnitude (e.g., $t(b'_n, b_{n+1}) = -0.35$ eV), the bands split at the X point (Supplementary Fig. 16e). The degree of splitting grows with the hopping amplitude, eventually leading to a substantial dispersion in the cyan band. When $t(b'_n, b_{n+1})$ reaches a sufficiently large value, such as -0.776 eV (Supplementary Fig. 16f), the cyan band overlaps with the red band, resulting in the metallic nature of CPHN **1** due to the band crossing the E_F . The metallic character of CPHN **1** results in a gapless spectrum, which prevents the definition of a quantized topological invariant. Consequently, symmetry-protected end states analogous to those in the SSH model—which relies on a finite bulk gap—cannot exist in this system. If just considering the aspect of symmetries, the lack of sublattice symmetry in CPHNs makes these systems trivial under standard Altland-Zirnbauer (AZ) classification^{5,6}.

Similarly, the SSH ladder model of CPHN **2** also consists of two coupled PPTL chains. However, the nature of the inter-chain interaction differs significantly from that in CPHN **1** due to the $Pmc2_1$ space group symmetry of CPHN **2** (Supplementary Fig. 17a,b). In the n th unit cell of CPHN **2**, the upper and lower PPTL chains are laterally shifted and indexed both in the same sequence of c–b–a and c'–b'–a' (left to right), respectively, highlighting the glide mirror symmetry of CPHN **2**. Based on the hopping terms specified in the figure caption, the resulting band structure from the SSH model (Supplementary Fig. 17d) shows good agreement with the DFT-calculated band structure (Fig. 3f, red solid curves). Compared to the hypothetical band structure of CPHN **2** without any inter-chain hopping (Supplementary Fig. 17c), the inclusion of inter-chain interactions primarily results in appreciable splitting of the upper red and lower blue dispersive bands. In contrast, the splitting of the flat (cyan) band remains minimal. This can be attributed to the absence of inter-chain hopping amplitudes between the central Wannier centers (specifically, $t(b_n, b'_{n+1})$ or $t(b_n, b'_n)$), which are associated with the green sites in Supplementary Fig. 17b and contribute predominantly to the nearly flat bands. As a result, the interaction between the nearly flat bands from the upper and lower PPTL chains remains weak, and the cyan band retains its flat character. Consequently, overlapping with the red band is not possible. Notably, CPHN **2** with the $Pmc2_1$ space group possesses a nonsymmorphic symmetry^{7,8}, which leads to the formation of symmetry-protected Dirac-like points at X point of the Brillouin zone.

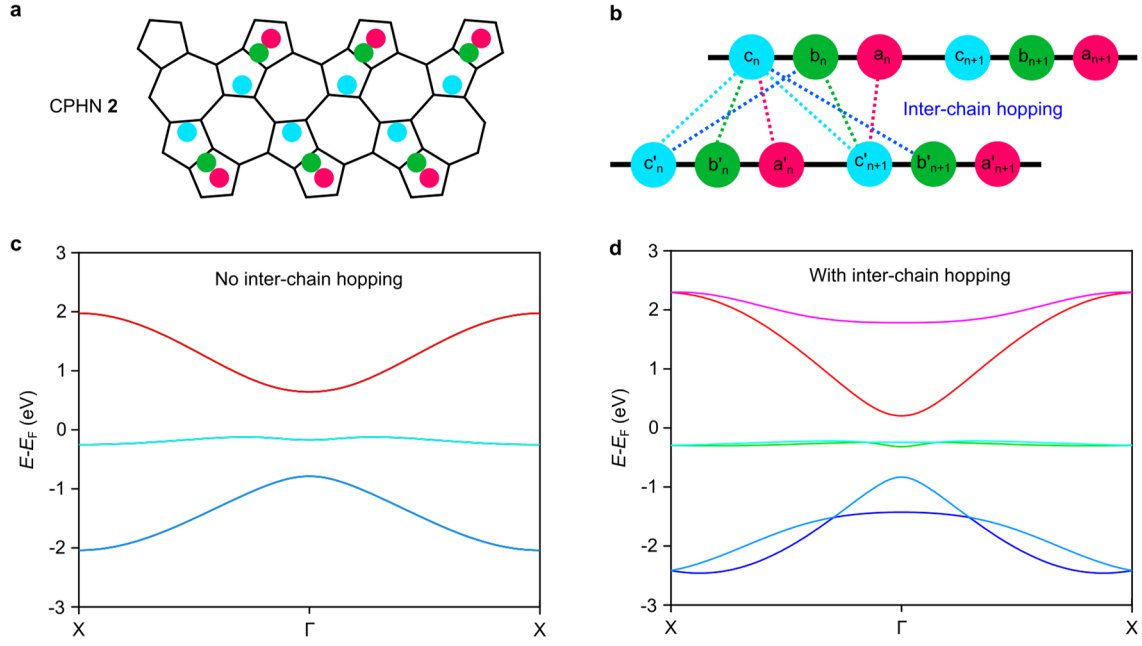


Supplementary Fig. 15 | Extended SSH model for PPTL. **a**, DFT-calculated band structure of PPTL (chemical structure shown in the inset). **b,c**, Projected contributions to the band structure from carbon atoms in red (**b**) and green (**c**) marked in the molecular structure. **d,e**, Carbon backbone of PPTL illustrating the positions of extracted Wannier centers (**d**) and the abstracted extended Su-Schrieffer-Heeger (SSH) tight-binding model with three lattice sites per unit cell with labeled hopping amplitudes (**e**). **f,g**, Band structures derived from the SSH model in **e**, with inclusion (**f**) and without inclusion (**g**) of the next-nearest neighbor hopping terms $t(c_n, b_{n+1})$, $t(b_n, a_{n+1})$, $t(c_n, c_{n+1})$. In **f**, three intracell hopping terms $t(a_n, b_n) = 0.127$ eV, $t(a_n, c_n) = 0.880$ eV, and $t(b_n, c_n) = 0.127$ eV, one nearest-neighbor intercell hopping term $t(c_n, a_{n+1}) = -1.147$ eV and three additional next-nearest neighbor intercell hopping terms $t(b_n, a_{n+1}) = -0.276$ eV, $t(c_n, b_{n+1}) = -0.258$ eV, and $t(c_n, c_{n+1}) = -0.214$ eV are also incorporated. The on-site energies of a , b and c sites are -0.25 eV, -0.05 eV, and -0.25 eV, respectively. In **g**, all the next-nearest neighbor intercell hopping terms are set to zero.



Supplementary Fig. 16 | Extended SSH ladder tight-binding model for CPHN 1. **a**, Carbon backbone of CPHN 1 showing the positions of the extracted Wannier centers. **b**, Extended SSH ladder tight-binding model comprising two coupled SSH chains based on the structure in **a**. Only inter-chain hopping parameters are labeled; the intra-chain hopping parameters for each PPTL chain are similar to those of an isolated PPTL. **c–f**, Band structures of CPHN 1 from the extended SSH ladder model in **b** with different intra- and inter-chain hopping parameters for comparison: In **c**, intra-chain hopping term: $t(a_n, b_n) = 0.221$ eV, $t(a_n, c_n) = -1.068$ eV, $t(b_n, c_n) = 0.002$ eV, $t(a_n, a_{n+1}) = -0.132$ eV, $t(b_n, b_{n+1}) = 0.176$ eV, $t(c_n, a_{n+1}) = 1.143$ eV, $t(c_n, b_{n+1}) = -0.471$ eV, $t(c_n, c_{n+1}) = -0.123$ eV. On-site energies: site a , -0.42 eV; site b , -0.356 eV; site c , -0.734 eV, where all inter-chain hopping terms are set to zero. In **d–f**, in addition to the intra-chain hopping terms in **c**, the following inter-chain hopping terms are included: $t(c'_n, b_n) = -0.374$ eV, $t(c'_n, c_n) = 0.854$ eV,

$t(c'_n, c_{n+1}) = -0.132$ eV, $t(b'_n, a_n) = -0.273$ eV, $t(b'_n, c_n) = 0.374$ eV, $t(b'_n, c_{n+1}) = -0.169$ eV, $t(a'_n, b_n) = 0.275$ eV, but setting $t(b'_n, b_{n+1}) = 0$ in **d** and $t(b'_n, b_{n+1}) = -0.35$ eV in **e** and $t(b'_n, b_{n+1}) = -0.766$ eV in **f**, respectively. The hopping amplitude $t(b'_n, b_{n+1})$ corresponds to the inter-chain hopping between green sites and marked by the green solid line in **b**, which governs the coupling strength between the cyan near- E_F flat bands, as in **c**, from the two decoupled PPTL chains.



Supplementary Fig. 17 | Extended SSH ladder tight-binding model for CPHN 2. **a**, Carbon backbone of CPHN 2 showing the positions of the extracted Wannier centers. **b**, Extended SSH ladder tight-binding model comprising two coupled SSH chains based on the structure in **a**. Only inter-chain hopping parameters are labeled; the intra-chain hopping parameters for each PPTL chain are similar to those of an isolated PPTL. **c,d**, Band structures of CPHN 2 from the extended SSH ladder model in **b** with different intra- and inter-chain hopping parameters for comparison: **(c)** Intra-chain hopping term: $t(a_n, b_n) \approx 0$ eV, $t(a_n, c_n) = 1.057$ eV, $t(b_n, c_n) = 0.162$ eV, $t(c_n, a_{n+1}) = -0.912$ eV, $t(b_n, a_{n+1}) = 0.140$ eV, $t(b_n, c_{n+1}) = 0.325$ eV, $t(c_n, b_{n+1}) = 0.191$ eV. On-site energies: site a , -0.122 eV; site b , -0.208 eV; and site c , 0.005 eV, where all inter-chain hopping terms are set to zero. **(d)** In addition to the intra-chain hopping terms in **c**, the following inter-chain hopping terms are included: $t(a_n, c'_{n+1}) = -0.504$ eV, $t(b_n, c'_n) = -0.906$ eV, $t(b_n, c'_{n+1}) = 0.118$ eV, $t(c_n, c'_n) = -0.264$ eV, $t(c_n, c'_{n+1}) = -0.264$ eV, $t(c_n, b'_n) = -0.118$ eV, $t(c_n, b'_{n+1}) = 0.906$ eV, $t(c_n, a'_n) = -0.504$ eV.

Supplementary Section 9: Origin of the zero-bias peaks in transport enhancements

The combined transport and local spectroscopy on the same CPHN **1** ribbon on Ag(111) (Supplementary Fig. 11) also demonstrate that the metallic character of CPHN **1** does not allow symmetry-protected end states as discussed in the following. The lifting experiment yields a high conductance of $\sim 0.4\text{--}0.8\ G_0$ over tip heights of 1–5 nm (Supplementary Fig. 11d), and the corresponding $I\text{--}V$ and dI/dV curves again show a pronounced enhancement near zero bias (Supplementary Fig. 11e,f), consistent with the junction calculations. In contrast, end-site dI/dV spectra do not show any zero-energy peak pinned at E_F at the terminal (Supplementary Fig. 11j,k). Moreover, the real-space dI/dV maps do not indicate a terminal-only state; instead, the ribbon interior retains strong spectral weight throughout the near- E_F energy window (approximately -130 meV to 140 meV, Supplementary Fig. 11i). Together, these observations are inconsistent with a sharply localized, termination-protected mid-gap boundary mode, and instead support a scenario in which the near- E_F transport enhancement is governed predominantly by electrode coupling and level alignment of bulk-like states as is discussed in the following.

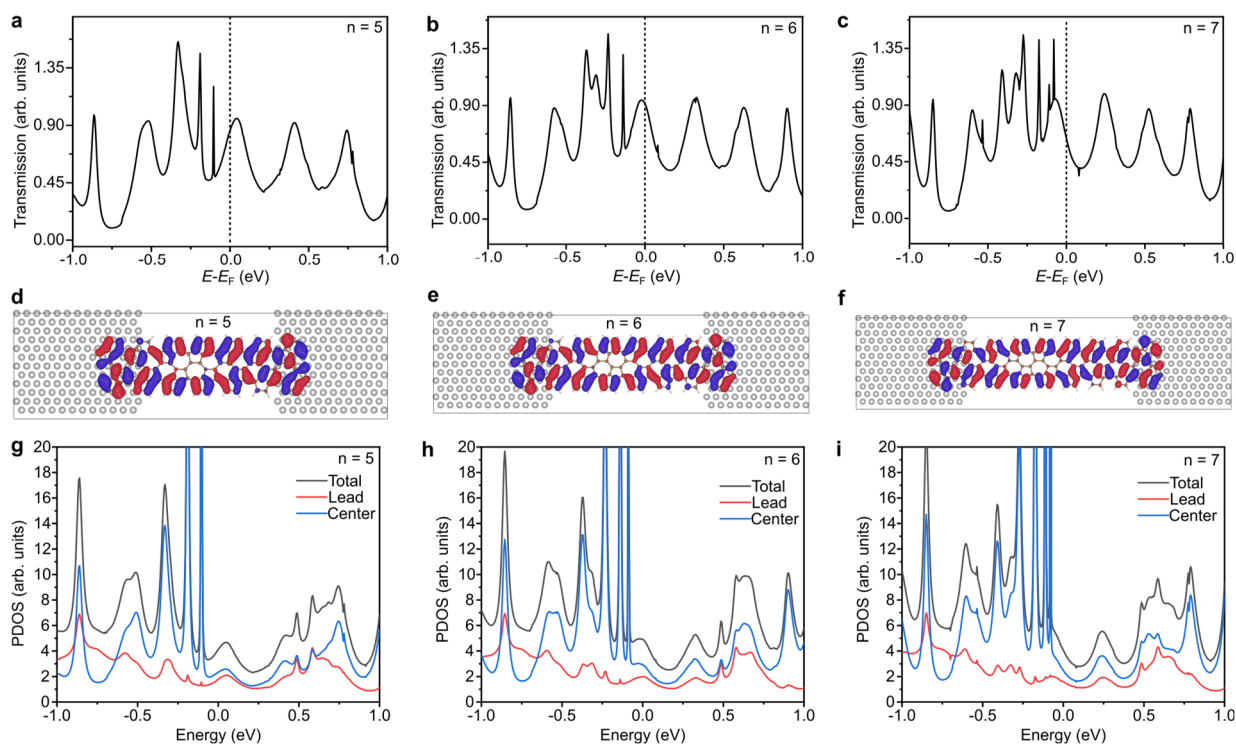
We performed DFT-based transmission calculations (Supplementary Fig. 18a–c) for two-electrode junctions containing 5 (~ 2.5 nm), 6 (~ 3.0 nm), and 7 (~ 3.5 nm) freestanding unit cells of CPHN **1** bridging two Ag(111) leads. All three junctions exhibit a pronounced transmission maximum in the near- E_F region, consistent with the experimentally observed high conductance around E_F (Fig. 2i and Supplementary Figs. 9i,j and 11f). Importantly, although the device length is varied, a B1-derived transmission feature remains close to E_F , suggesting that electrode coupling can shift and broaden QWS-derived resonances into the near- E_F region.

To test the influence of electrode-overlap length more directly, we further performed additional transport calculations with the freestanding CPHN **1** segment length fixed at six unit cells, while the number of CPHN **1** units overlapping with the right Ag electrode was varied from one to three and four (Supplementary Fig. 19). We then performed complementary calculations with the total ribbon length fixed while progressively reducing the right-electrode overlap, thereby increasing the length of the freestanding segment (Supplementary Fig. 20). The latter geometry better approximates the lifting experiment, in which a finite portion of the ribbon can remain adsorbed on the Ag(111) substrate/electrode. Both sets of calculations show that a B1-derived transmission resonance remains close to E_F for different right-electrode overlap lengths, although its precise energy shifts with the

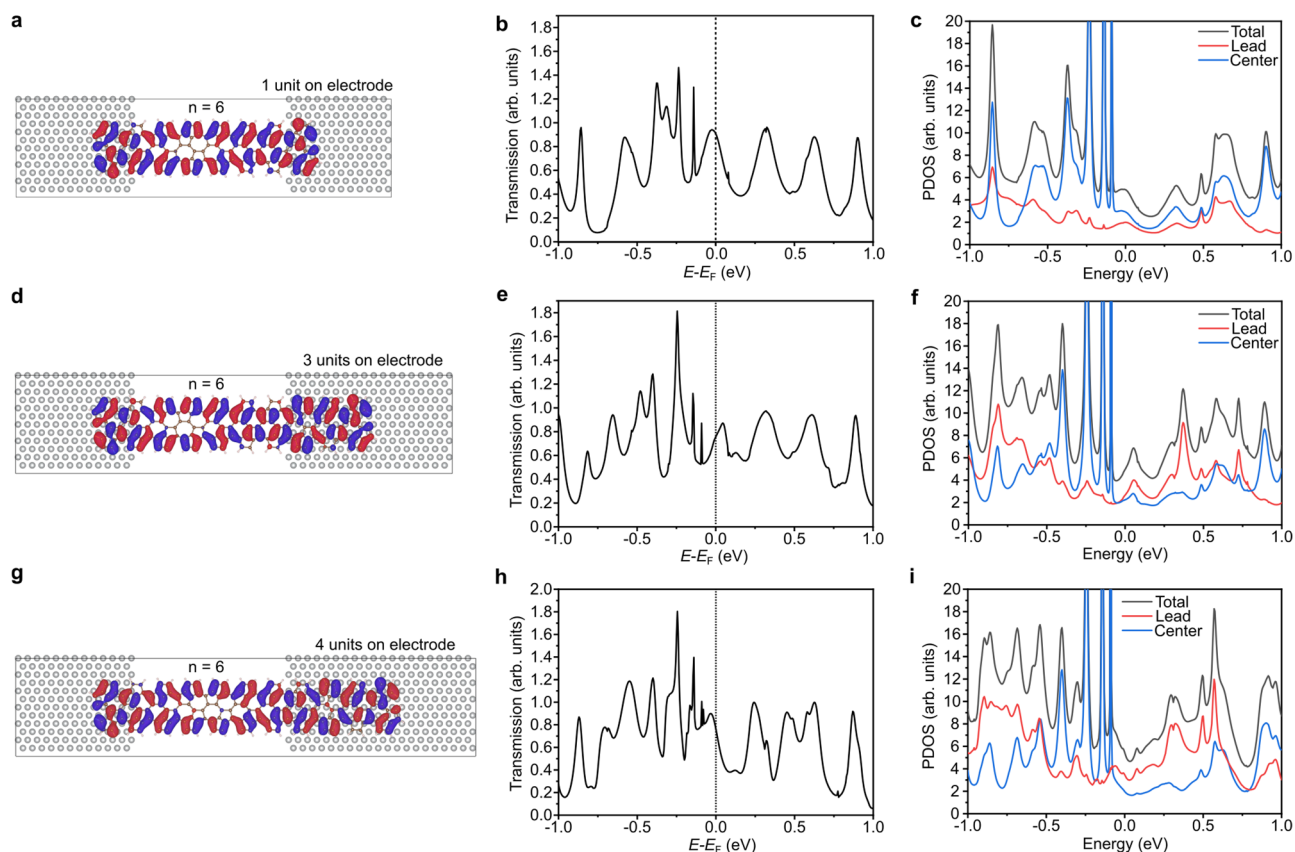
contact geometry, consistent with changes in electrode coupling and charge transfer. These results support a contact-induced near- E_F level-alignment scenario rather than a definitive proof of strict Fermi-level pinning.

To identify the states responsible for this feature, we analyzed the projected density of state (PDOS) and wavefunctions (Supplementary Figs. 18–20). The near- E_F transmission resonance is derived from a B_1 -band quantum-well state (QWS), whose wavefunction is spatially extended over the CPHN **1** backbone. Notably, in the STS measurements of CPHN **1** on Br/Ag(111) (Fig. 4e,g), the E_F may position between two adjacent QWS states. Upon contact with Ag electrodes, charge transfer and hybridization can shift and broaden the QWS-derived resonances, providing a plausible explanation for the broad near-zero-bias conductance enhancement observed in the transport measurements, analogous to contact-induced level-alignment effects reported in polyene junctions⁹.

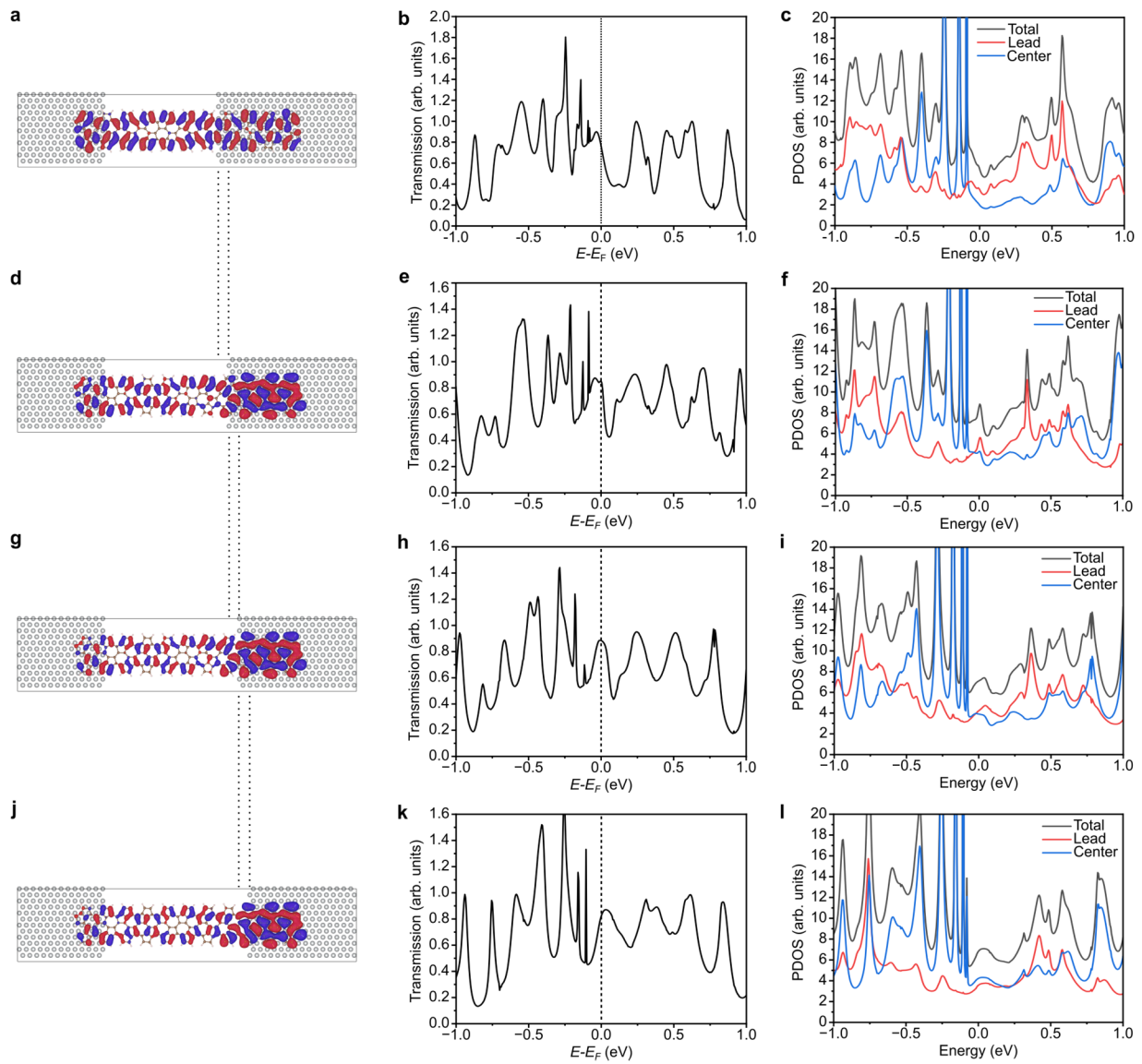
This interpretation is further supported by the projected DOS analysis (Supplementary Figs. 18g–i, 19c,f,i and 20c,f,i,l), which shows prominent near- E_F DOS features. These features are not dominated by the ribbon termini on the metal leads; instead, they retain substantial weight on the central freestanding segment (blue curves) and are notably larger than the contribution from the lead-adsorbed parts (red curves). Together, these results support a picture in which the high transmission around E_F originates from electrode-driven alignment and coupling of extended QWS-derived states, rather than from an end-localized mode.



Supplementary Fig. 18 | DFT calculation of electron transmission and density of states in a two-electrode device. The adsorption geometry of CPHN **1** on the Ag(111) electrodes was constructed based on the optimized CPHN **1**/Ag(111) model shown in Extended Data Fig. 6b. **a–c**, Electron transmission spectra of the device with 5 (**a**), 6 (**b**), and 7 (**c**) unit cells of the CPHN **1** structure between the two leads, as depicted in panels **d–f**. **d–f**, Wavefunctions of the band B₁-derived quantum well states of the CPHN **1** near E_F . **g–i**, Total density of states (black lines) for the CPHN **1** chains in the device configurations shown in panels **d–f**, respectively. For comparison, the projected DOS contributions from the central freestanding segment (Center, blue lines) and the segments adsorbed on the Ag(111) leads (Lead, red lines) are also shown.



Supplementary Fig. 19 | Transport calculations for CPHN 1 junctions with different electrode-overlap lengths. The data in **a–c** are identical to those shown in Supplementary Fig. 18b,e,h and are duplicated here for direct comparison with the different right-electrode overlap lengths. **a,d,g**, Device geometries and wavefunctions of the near- E_F B₁-derived quantum-well states for CPHN 1 junctions with the same freestanding segment length of six unit cells between the two Ag electrodes, but with one, three and four CPHN 1 units overlapping with the right Ag electrode, respectively. **b,e,h**, Corresponding electron transmission spectra for the device configurations shown in **a,d,g**, respectively. A B₁-derived transmission resonance remains close to E_F for different right-electrode overlap lengths, although the peak is not exactly fixed at zero energy. **c,f,i**, Total density of states (black curves) of the CPHN 1 chains in the corresponding junctions. For comparison, the projected DOS contributions from the central freestanding segment and from the segments adsorbed on the Ag(111) electrodes are also shown. The results support a contact-induced near- E_F level-alignment scenario, in which electrode coupling and charge transfer can shift and broaden B₁-derived QWS resonances near E_F .



Supplementary Fig. 20 | Transport calculations for CPHN 1 junctions with a fixed total ribbon length and varying right-electrode overlap lengths. **a–c**, Data reproduced from Supplementary Fig. 19g–i for comparison. **d,g,j**, Device geometries and wavefunctions of the near- (E_F) (B_1)-derived QWSs. The total ribbon length is fixed in all four configurations; relative to **a**, the ribbon-facing edge of the right Ag electrode is retracted along the ribbon axis by 2, 4, and 6 Ag atomic columns in **d**, **g**, and **j**, respectively, thereby progressively decreasing the electrode overlap and increasing the freestanding ribbon length. **e,h,k**, Corresponding transmission spectra. **f,i,l**, Total and projected densities of states of the freestanding and electrode-supported segments. The (B_1)-derived resonance remains near (E_F) but shifts with the electrode overlap because of contact-induced coupling and charge transfer, consistent with the differential-conductance peak shifts observed in Fig. 2i and Supplementary Figs. 9i,j and 11f.

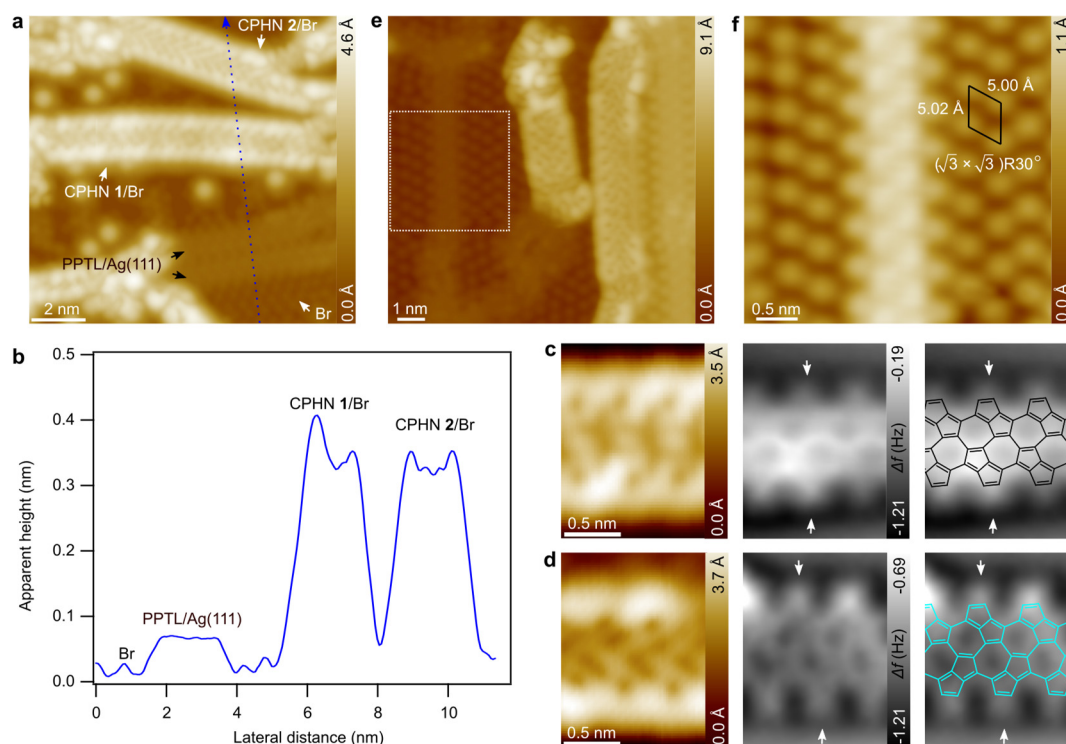
Supplementary Section 10. Decoupling CPHN 1 and 2 on Ag(111) surface by Br intercalated adlayer

To decouple the CPHNs from the Ag(111) surface, we performed a post-treatment of the prepared samples of CPHN 1 and 2 on Ag(111) by dosing 1,2,5,6-tetrabromocyclooctane (a pressure of 1×10^{-8} mbar) from a glass container (300 K) as bromine source to the CPHN/Ag(111) sample held at 400 K. Since the cyclooctane backbone desorbs completely from Ag(111) at 400 K, only Br remains chemisorbed on the surface and forming close-packed Br adlayer between the CPHNs and Ag(111) surface. Such post-treatments led to the formation of floated CPHNs (Supplementary Figs. 21 and 22), indicating that the Br adlayer should be inserted between the CPHNs and the Ag(111) substrate. This is demonstrated by its apparent height of around 0.3 nm higher than the Br adlayer on Ag(111) as illustrated by the line profile in Supplementary Fig. 21b. In comparison, the PPTL chains merged into the Br adlayer as shown by the STM images in Supplementary Fig. 21e,f and their slightly higher apparent height (0.03 nm) than the Br adlayer, indicating that the PPTL chains should be more strongly adsorbed on Ag(111) than the CPHNs.

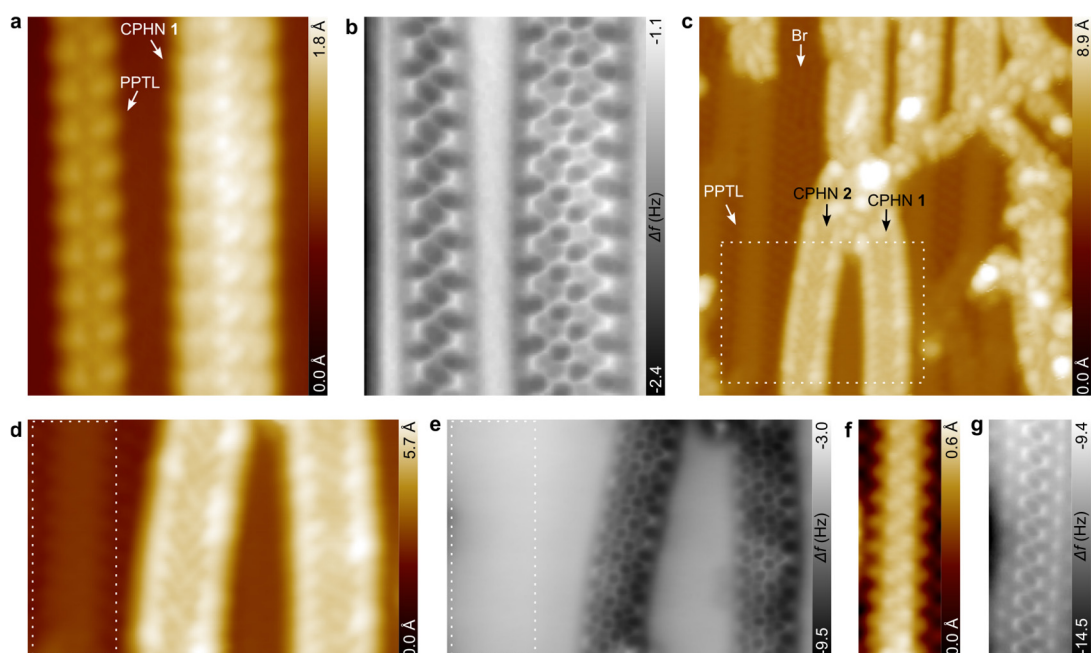
The adsorption of CPHNs on Br adlayer and PPTL on Ag(111) is further confirmed by the constant-height nc-AFM imaging of the CPHNs/Br and PPTL/Ag(111) simultaneously. As shown by Supplementary Fig. 22a,b, the STM and corresponding nc-AFM images of PPTL and CPHN 1 adsorbed on Ag(111) reveal nearly identical adsorption heights. However, after Br intercalation, the CPHNs exhibit significantly greater apparent heights in the STM image (Supplementary Fig. 22c). The zoom-in STM (Supplementary Fig. 22d) and nc-AFM (Supplementary Fig. 22e) images of the white-framed region in Supplementary Fig. 22c show that only CPHN 1 and 2 remain visible in the constant-height nc-AFM image at a tip height of 10 pm. Notably, while PPTL is visible in the constant-current STM image, it becomes completely invisible in the constant-height nc-AFM image, indicating that the adsorption height of CPHNs is much greater than that of PPTL. This stands in stark contrast to their similar adsorption heights on Ag(111) prior to Br intercalation. Furthermore, a zoom-in nc-AFM image of PPTL at a tip height of -240 pm (Supplementary Fig. 22g) quantifies the lifted adsorption height of CPHNs after Br intercalation as 250 pm. These experimental observations provide strong evidence for the presence of Br adatoms beneath the CPHNs.

The nc-AFM images for the floated CPHN 1 and 2 have also been measured using Br-decorated tip (Supplementary Fig. 21c,d) and CO-functionalized tip (Supplementary Fig. 22e) for their

distinguishment. The Br adlayer adopted a structure of $(\sqrt{3} \times \sqrt{3})R30^\circ$ (Supplementary Fig. 21e,f), which is similar to the reported structure of 1/3 monolayer Br adlayer on Ag(111) in previous work¹⁰. Owing to the co-adsorption with PPTL chains, minor defects in the intercalated Br layer may occur leading to the slightly inhomogeneous adsorption of CPHNs on Br layer. It is noticed that the relatively bright spot in STM images of CPHNs (Fig. 4b,c, Fig. 4j,k, and Supplementary Fig. 22c,d) can be inhomogeneous from those defects in Br intercalation layer, since their AFM images (Fig. 4d, Fig. 4l, and Supplementary Fig. 22e) indicate most of the bright spots in STM images do not present as defects in bulk of CPHNs except existence of a certain defect at the connection sites (CPHN segment ends). The 1,2,5,6-Tetrabromocyclooctane molecule was purchased from commercial company with purity >98%.



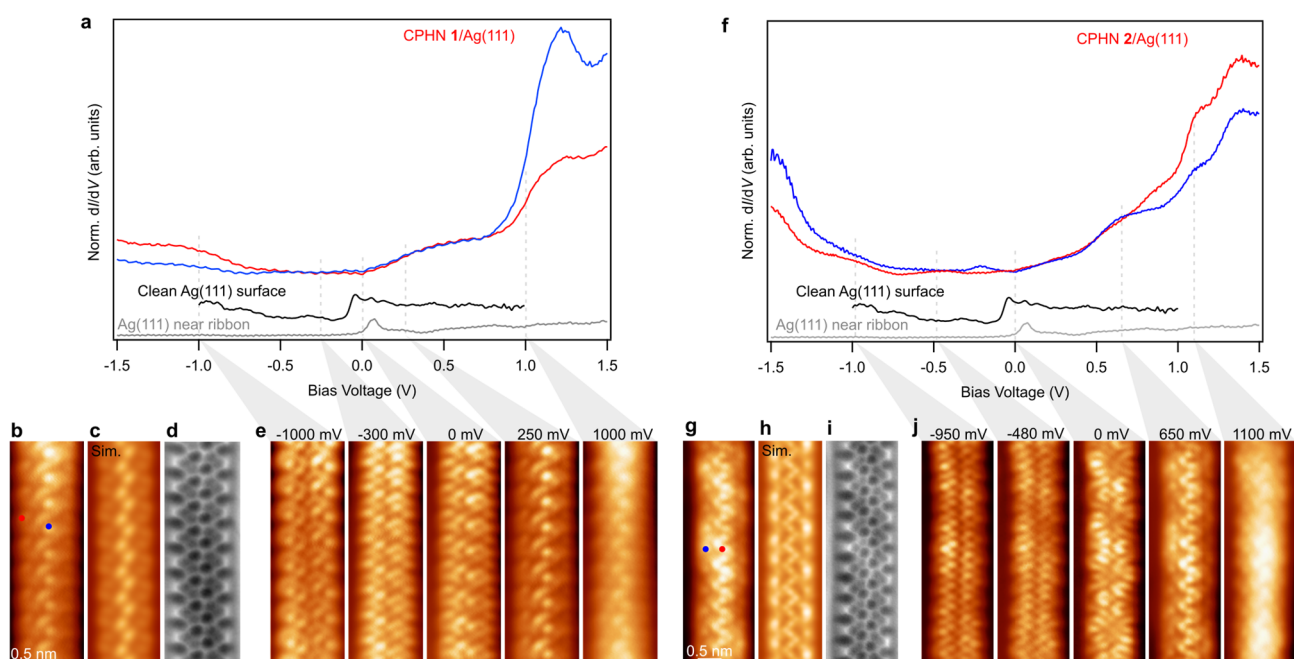
Supplementary Fig. 21 | Insertion of Br adlayer between CPHNs and Ag(111). **a**, Overview STM image (-1.0 V and 10 pA) taken after dosing 1,2,5,6-tetrabromocyclooctane as bromine source to the CPHNs/Ag(111) sample held at 400 K. **b**, Line profile along the blue dashed line in **a**, showing the floated feature of CPHNs **1** and **2**. **c,d**, STM (left) and nc-AFM images (middle) of the floated CPHNs **1** and **2** recorded with Br-decorated tips respectively, with the superposed structural model on the AFM image (right). The arrows indicated the positions of outermost five-membered rings. STM imaging conditions of -0.4 V and 10 pA in **c**, and -1.0 V and 10 pA in **d**. **e**, STM image (-1.0 V and 10 pA) showing the floated CPHNs on Br/Ag(111) and Br island. **f**, Magnified STM image (-1.0 V and 10 pA) of the white dashed frame in **e** showing the embedment of PPTL chain in the Br adlayer island. The adsorption of $(\sqrt{3} \times \sqrt{3})R30^\circ$ Br adlayer by locating Br atoms at the hollow sites of Ag(111) could be derived. Noteworthy, the PPTL chains adsorb more strongly than the CPHNs on Ag(111) surface. Most of the PPTL chains still sit on the Ag(111) surface, leading to an apparent height similar to that of the Br adlayer.



Supplementary Fig. 22 | Comparison of the adsorption heights of CPHNs and PPTL before and after the Br intercalation. **a,b**, STM and nc-AFM images of the adjacently adsorbed PPTL and CPHN **1** on Ag(111) surface before Br intercalation recorded with CO-functionalized tip. **c**, Large-scale STM image of the sample in **a** after Br intercalation, recorded with Br-functionalized tips. **d,e**, Zoom-in STM and nc-AFM images of the white framed region in **c**. **f,g**, Zoom-in STM and nc-AFM images of the white framed region in **d**. The STM images in **c** and **d** are recorded with Br-functionalized tips; The STM and nc-AFM images in **e–g** are recorded with CO-functionalized tips. The constant-height nc-AFM images in **e** and **g** are recorded at heights of 10 pm and –240 pm respectively with respect to the STM setpoint of –5 mV, 20 pA on the CPHN **2**. Figure sizes in **a,b**, $5 \times 3.71 \text{ nm}^2$; in **c**, $13 \times 13 \text{ nm}^2$; in **d,e**, $6.7 \times 4.3 \text{ nm}^2$; in **f,g**, $1.5 \times 4.3 \text{ nm}^2$. Tunneling parameters for the STM images in **a,c,d**, –1.0 V, 20 pA.

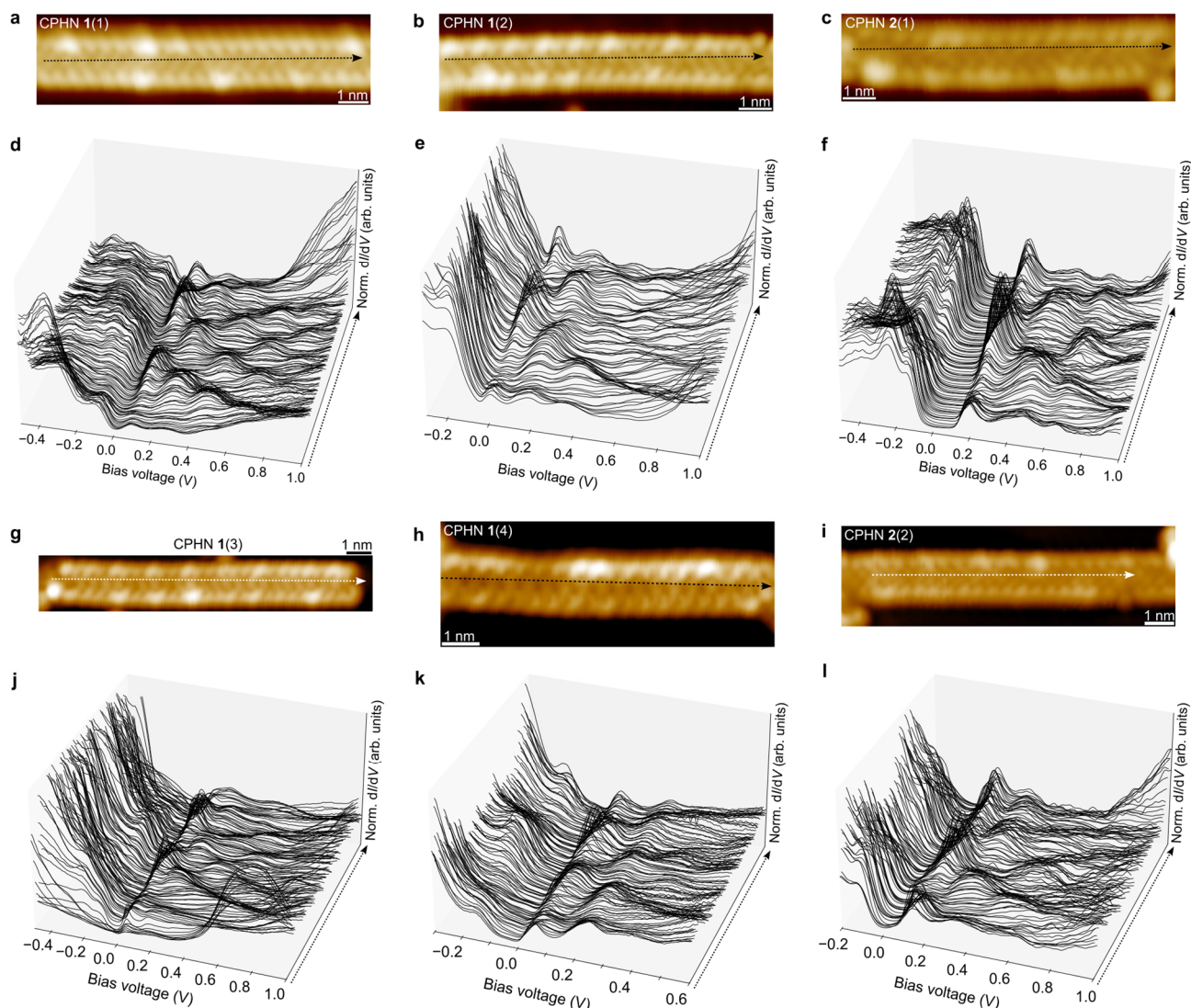
Supplementary Section 11. Scanning tunnelling spectroscopic (STS) measurements of CPHNs 1 and 2 on Ag(111) surface

To characterize the electronic properties of CPHN **1** and **2**, we first performed the STS measurements of CPHN **1** and **2** directly on Ag(111) surface, as shown in Supplementary Fig. 23. The normalized dI/dV spectra at the center and side of CPHN **1** is displayed in Supplementary Fig. 23a, showing apparent step-like features at -1.0 V, 0.25 V and 1.0 V. The corresponding dI/dV maps in Supplementary Fig. 23e exhibit prominent distributions of DOSs located at the edge and center for the occupied and unoccupied states of CPHN **1**, respectively. However, due to the strong coupling between CPHN **1** and Ag(111) substrate, the intrinsic electronic structure of CPHN **1** was not resolved in the dI/dV spectra (Supplementary Fig. 23a), even though the hybridized states showed a certain spatial distribution (Supplementary Fig. 23e), where the dI/dV measurements were performed at setpoint conditions of 0.0 V and -0.3 V. Similarly, due to the strong coupling between CPHN **2** and Ag(111) substrate, the dI/dV spectra (Supplementary Fig. 23f) and dI/dV maps (Supplementary Fig. 23j) did not show the intrinsic electronic structure for CPHN **2**. As comparison, the DFT-calculated bands structures of CPHN **1** and **2** on Ag(111) surface obviously shift downwards by 0.6 and 1.0 eV (Extended Data Fig. 6b,e), respectively with respect to those of freestanding CPHN **1** and **2**, indicating a considerable charge transfer from the Ag(111) surface to the CPHNs.

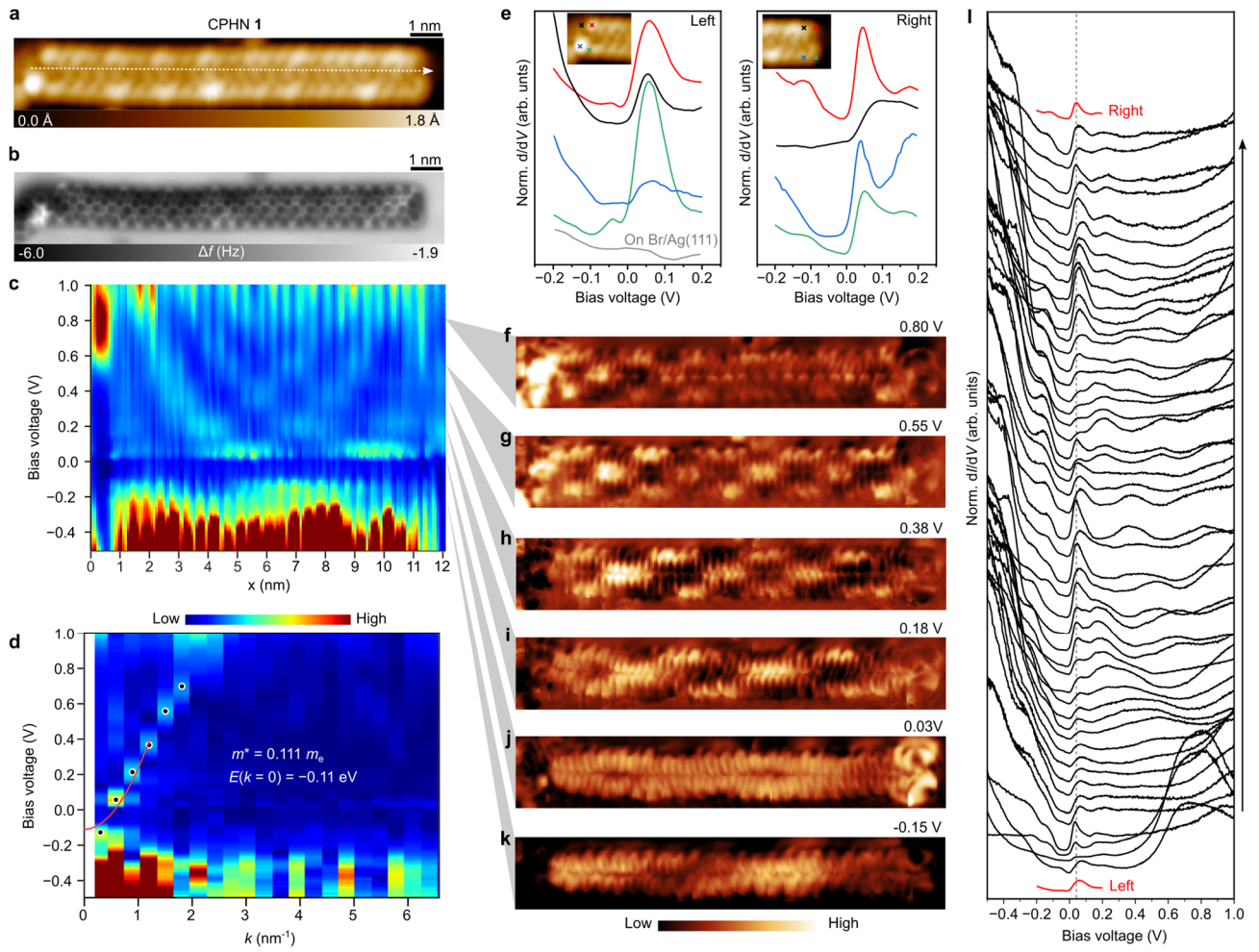


Supplementary Fig. 23 | STS measurements of CPHN 1 and 2 on Ag(111). **a,f**, Typical normalized dI/dV spectra for CPHN 1 and 2 on Ag(111). The red and blue dI/dV spectra for CPHN 1 and 2 on Ag(111) taken at the positions marked with correspondingly colored dots on the STM images in **b** and **g**, respectively. The black and gray curves show the dI/dV spectra recorded on a clean Ag(111) surface and a bare Ag surface region near CPHNs. The shift (from -0.1 V to 0.1 V) in the Ag(111) surface states is due to the confinement effect induced by the high coverage of CPHNs and PPTL chains on the Ag(111) surface. **b,c**, Experimental and simulated STM topographic images of CPHN 1 on Ag(111), respectively. **d**, Nc-AFM image of CPHN 1 on Ag(111), correspondingly within the same area as in **b**. **e**, Corresponding dI/dV maps at indicated bias voltages of CPHN 1 on Ag(111). **g,h**, Experimental and simulated STM topographic images of CPHN 2 on Ag(111), respectively. **i**, Nc-AFM image of CPHN 2 on Ag(111), correspondingly within the same area as in **g**. **j**, Corresponding dI/dV maps at indicated bias voltages of CPHN 2 on Ag(111). The STM topographic images and dI/dV maps were recorded using a constant-height mode using a cleaned tungsten tip. The nc-AFM images were recorded using a CO-functionalized tip at constant-height mode. A lock-in preamplifier was used in taking dI/dV spectra and maps with sinusoidal modulations of 10 mV (peak-to-peak) at 973 Hz. The spectra are shifted for clarity. The tunneling parameters of the STM images: in **b**, 1.0 V, 10 pA; in **g**, 0.9 V, 10 pA.

Supplementary Section 12. 3D views of several complete data sets of dI/dV spectrum for CPHNs 1 and 2 on Br/Ag(111) surface (decoupled CPHN 1 and 2) in different samples



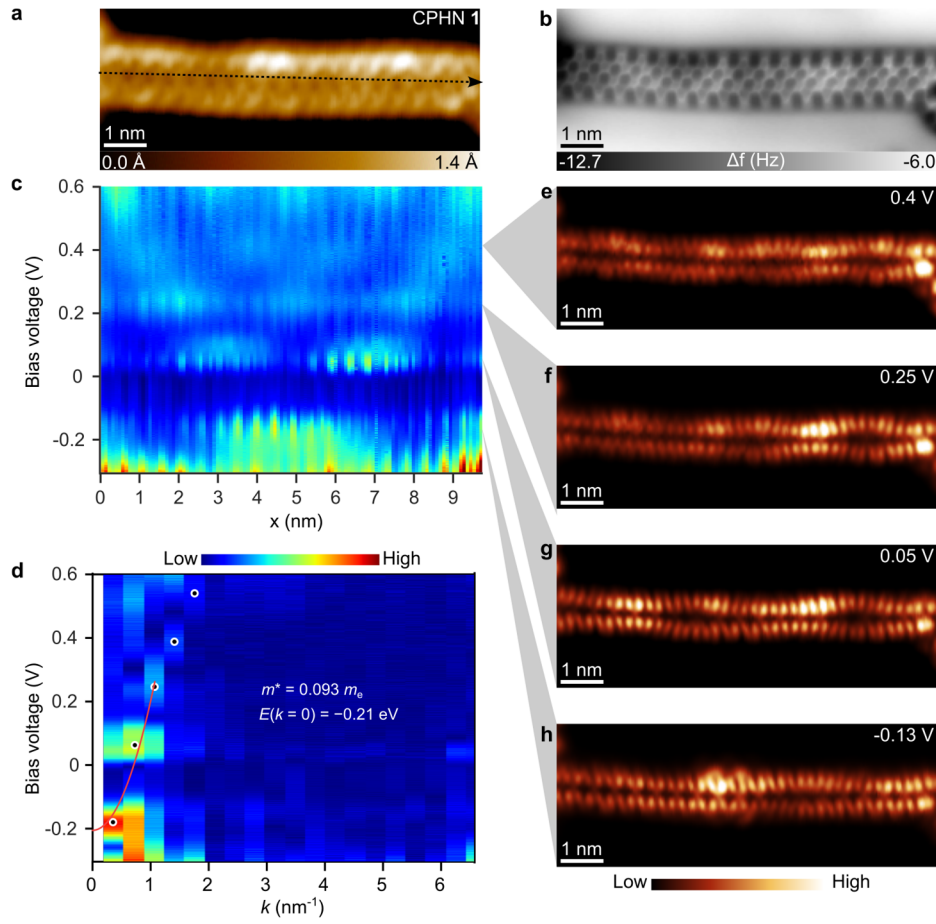
Supplementary Fig. 24 | 3D views of stacked dI/dV spectra of CPHNs. **a–c,g–i**, STM images (-1.0 V, 20 pA) of four CPHN 1 ribbons numbered 1 (**a**), 2 (**b**), 3 (**g**), 4 (**h**) and two CPHN 2 ribbons numbered 1 (**c**), 2 (**i**). CPHN 1(1–4) and CPHN 2(1,2) are identical to those shown in Fig. 4c, Extended Data Fig. 9a, Supplementary Figs. 25,26a, Fig. 4k, Supplementary Fig. 27a, respectively. **d–f,j–l**, Stacking of normalized dI/dV spectra recorded along the arrowed line grids in **a–c,g–i**, with equidistant 170, 100, 128 128, 150, and 128 points, plotted in a 3D view, respectively. Complete datasets are also presented as stacked 2D LDOS maps in Fig. 4e, Extended Data Fig. 9b, Supplementary Figs. 25,26c, Fig. 4m, and Supplementary Fig. 27c, respectively.



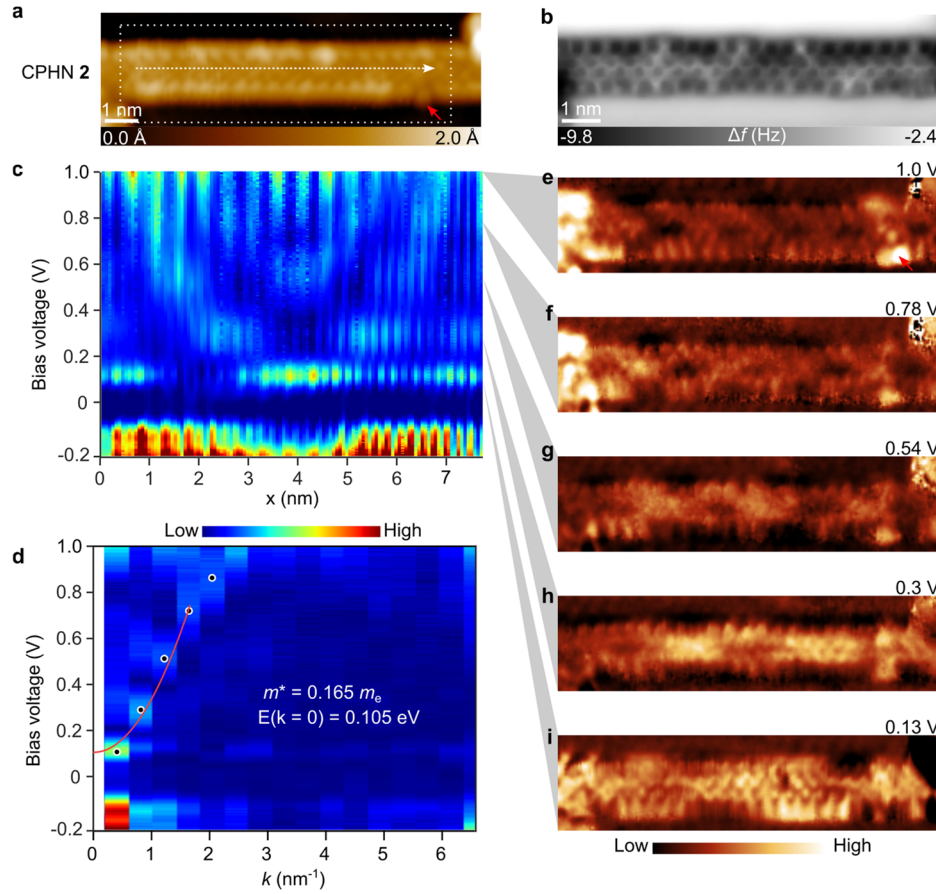
Supplementary Fig. 25 | QPI characterization of a CPHN 1 ribbon with a truncated terminus.

a, STM image of a CPHN 1 ribbon featuring a truncated right-hand terminus, acquired with a CO-functionalized tip. **b**, nc-AFM image of the region outlined by the white frame in **a**. **c**, Normalized 2D LDOS map (dI/dV line-grid) recorded along the direction indicated by the arrow in **a**. **d**, FT-LDOS obtained from the dataset in **c**, displayed within the first Brillouin zone. Fitted band (red curve) using parabolic relation $E(k) = E(k=0) + \frac{\hbar^2}{2m^*}k^2$ is overlaid. **e**, Normalized dI/dV point spectra acquired at the colored cross positions on the left and right terminus of the CPHN 1 ribbon in **a** (shown in the inset). **f–k**, Bias-dependent constant-current dI/dV maps of the same ribbon (region in **b**) recorded at the voltages indicated in the panels, revealing energy-dependent standing-wave patterns. **l**, Normalized dI/dV spectra recorded along the arrowed line grids with equidistant 150 points, plotted with every 3rd spectrum shown (skipping 2 spectra) and vertically offset for clarity. Complete dataset is presented as stacked 2D LDOS maps in panel **c**, with additional 3D views in Supplementary Fig. 24j. The two red spectra labeled “left” and “right” are identical to the two spectra shown in panel **e**, which show their dominant origin as QWS tails at the terminals. STM Imaging

parameters: **a**, $U = -1.0$ V, $I = 20$ pA. **b**, z -offset = 0 pm with respect to the STM set point of (-10 mV, 20 pA).



Supplementary Fig. 26 | QPI characterization of an additional CPHN 1 ribbon. **a,b**, STM (**a**) and nc-AFM (**b**) images of a CPHN 1 ribbon acquired with a CO-functionalized tip. **c**, Normalized 2D LDOS map (dI/dV line-grid) recorded along the direction indicated by the arrow in **a**. **d**, FT-LDOS obtained from the dataset in **c**, displayed within the first Brillouin zone. Fitted band (red curve) using parabolic relation $E(k) = E(k=0) + \frac{\hbar^2}{2m^*} k^2$ is overlaid. The parabolic fit is included only as a guide to the local low- k curvature; the limited number of points reflects the finite ribbon length and the restricted validity of the quadratic approximation near Γ . **e–h**, dI/dV maps of the same CPHN 1 ribbon recorded at the bias voltages indicated in the panels, revealing energy-dependent standing-wave patterns. Imaging parameters: **a**, $U = -1.0$ V, $I = 20$ pA. **b**, z -offset = 0 pm with respect to the STM set point of (−10 mV, 30 pA).



Supplementary Fig. 27 | QPI characterization of an additional CPHN 2 ribbon. **a**, STM image of a CPHN 2 ribbon acquired with a CO-functionalized tip. One defect at the right side is marked with red arrow. **b**, nc-AFM image of the region marked by the white frame in **a**. **c**, Normalized 2D LDOS map (dI/dV line-grid) recorded along the direction indicated by the arrow in **a**. **d**, FT-LDOS obtained from the dataset in **c**, displayed within the first Brillouin zone. Fitted band (red curve) using parabolic relation $E(k) = E(k=0) + \frac{\hbar^2}{2m^*} k^2$ is overlaid. **e-i**, Constant-current dI/dV maps of the same CPHN 2 ribbon in panel **b** recorded at the bias voltages indicated in the panels, revealing energy-dependent standing-wave patterns. Imaging parameters: **a**, $U = -1.0$ V, $I = 20$ pA. **b**, z -offset = 0 pm with respect to the STM set point of (−10 mV, 20 pA)

Supplementary Section 13. Effect of the finite lengths and different termini

The assignment of the band onset is based on the combined analysis of real-space STS maps and FT-LDOS patterns. For CPHN **1**, the first-envelope QWS feature of the B1-derived manifold is observed below E_F , indicating that this manifold spans E_F . For CPHN **2**, the corresponding first unoccupied QWS feature remains above E_F , with no occupied continuation below E_F , consistent with a gapped band structure. The parabolic fits are therefore used only as approximate guides to the local band curvature and band-minimum position, rather than as the sole criterion for metallic or semiconducting assignment.

We observe that the band minimum position varies among samples. In some cases, the metallic band (B₁) minimum of Br-decoupled CPHN **1** with a similar length of about 20 repeating units coincidentally aligns with the E_F , resulting in a momentum-dependent peak feature at the E_F in the dI/dV spectra (Extended Data Fig. 9d and Supplementary Fig. 24e). The variation in band minima across different samples can likely be attributed to either sample-dependent doping levels (possibly due to defects in the Br adlayer) or the connection structures between CPHN **1** segments and other species at their ends. Our simulations indicate that the position of band minimum in finite-length freestanding CPHN **1** show dependence on the different termini used (Extended Data Fig. 9e–j), indirectly showing the possible effect from the connection structures at the ends of CPHN **1**. Additionally, our calculations on longer freestanding CPHNs (40 repeating units) confirm their metallic (CPHN **1**) and semiconducting (CPHN **2**) properties (Supplementary Fig. 29). The simulated band structures closely match the calculated results from 1D crystals of CPHN **1** and CPHN **2** (Fig. 4a,i). The band folding observed in the DFT-calculated FT-LDOS (dashed lines, Supplementary Fig. 29e,j) arises intrinsically from the quasiparticle interference (QPI) technique, as previously reported

in the literature¹¹. Comparison with shorter CPHNs reveals that band energy positions are also length dependent.

For finite CPHN segments, the STS resonances represent quantum-well states whose energies depend on ribbon length, termini and local electrostatic environment; therefore, finite-size level spacings should not be directly interpreted as band gaps of the corresponding infinite ribbon. We also note that a relatively homogeneous gap-like suppression around E_F is observed in several finite CPHN **1** segments. This feature should not be interpreted as a single-particle band gap of the infinite CPHN **1**. In finite, partially decoupled one-dimensional segments probed by STM/STS, the measured resonances correspond to electron addition/removal processes and can be influenced by addition-energy and local electrostatic effects, including possible Coulomb-charging contributions, as known for supported metallic nano-objects in STM junctions¹². These effects, superimposed on ordinary finite-size QWS quantization, can enlarge the apparent spacing between the highest occupied and lowest unoccupied QWS near E_F . Therefore, the near- E_F suppression observed in finite CPHN **1** segment does not contradict the FT-LDOS/QPI evidence that the QWS manifold spans E_F , nor the conclusion that CPHN **1** has a metallic band crossing in the long-ribbon limit.

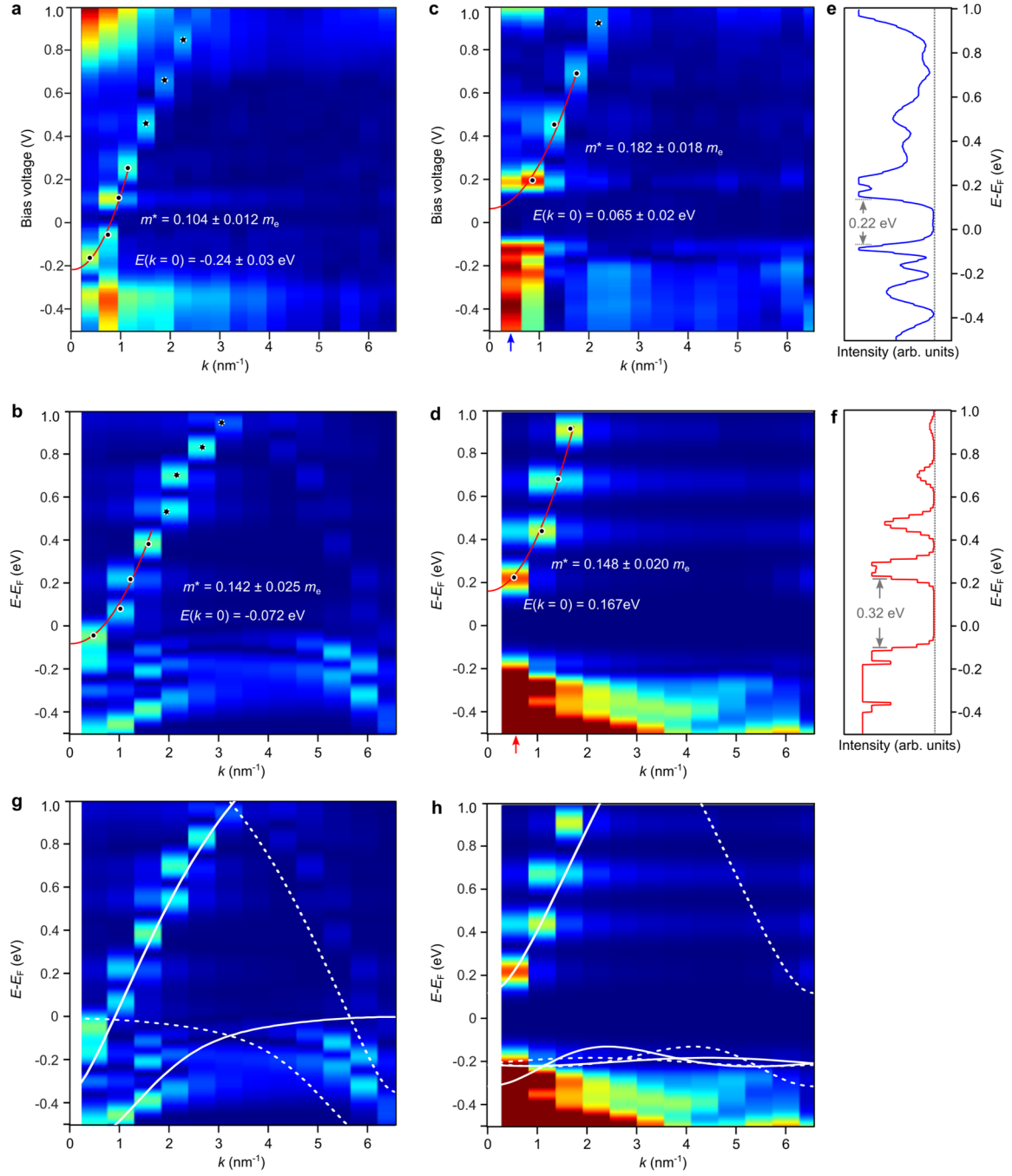
In the dI/dV spectra and FT-LDOS maps, the VHS states are not obviously observed. This can likely be assigned to the presence of VHS states away from the highly symmetric Γ and X points in finite-length CPHN **1**, making these VHS states less sensitive to be detected in the dI/dV measurements. Note that the numerically derived differential conductance in the transport measurements is mechanistically different from the dI/dV spectra. Compared to the simulated FT-LDOS, the lack of intensity for $k > 3 \text{ nm}^{-1}$ in experimental FT-LDOS is mainly caused by the resolution limit due to finite tip-sample separation and tip size, similar to that reported previously¹¹.

To demonstrate the reproducibility of the FT-LDOS (QPI) analysis beyond the representative datasets shown in Fig. 4, we additionally performed independent QPI measurements on defect-free segments of both CPHN **1** and CPHN **2** with lengths comparable to those analyzed in the main text. The additional CPHN **1** dataset (Supplementary Fig. 26) again exhibits clear finite-size quantization of quantum-well states, with multiple discrete levels spanning across E_F and level spacings comparable to those extracted in Fig. 4, as expected for standing waves in a finite one-dimensional conductor. Likewise, the additional CPHN **2** dataset (Supplementary Fig. 27) reproduces a semiconducting dispersion and yields a transport/STS gap of approximately ~ 0.18 eV, close to the ~ 0.22 eV obtained from the dataset shown in Fig. 4o. Together, these additional measurements confirm that the key FT-LDOS signatures, finite-size quantum well states quantization for CPHN **1** and a gapped dispersion for CPHN **2**, are robust and reproducible across independently prepared ribbons and measurement locations.

To further assess how finite length and termination structures affect the near- E_F electronic signatures, we performed FT-LDOSs on another Br-decoupled CPHN **1** ribbon on Br/Ag(111) that features a truncated right-hand terminus (Supplementary Fig. 25a,b). The line-grid STS map along the ribbon (Supplementary Fig. 25c) does not show any pronounced zero-bias state that is spatially confined to the truncated right terminus or the left terminus. Although the constant-current dI/dV map recorded at $U = 0.03$ V exhibits enhanced intensity near the right terminus (Supplementary Fig. 25j), the corresponding point spectra (Supplementary Fig. 25e) demonstrates that this signal is consistent with the tail of a quantum-well state centered at ~ 0.03 V, rather than a state pinned at E_F . Importantly, the LDOS maps and FT-LDOS analysis again reveal a metallic band crossing E_F that is very similar to what we observe for other CPHN **1** ribbon, despite the fact that the termination of this ribbon differs from that in Fig. 4c and Supplementary Fig. 26. Together with the termination-dependent band-

minimum shifts discussed above, these data support the view that the detailed near- E_F spectral weight and band-edge positions can vary with ribbon length and end/connection structures, while the overall metallic dispersion of CPHN **1** remains robust; notably, the observed end-enhanced intensity at specific finite bias is naturally accounted for finite-size standing-wave (QWS) tails rather than a termination-protected, zero-energy end mode.

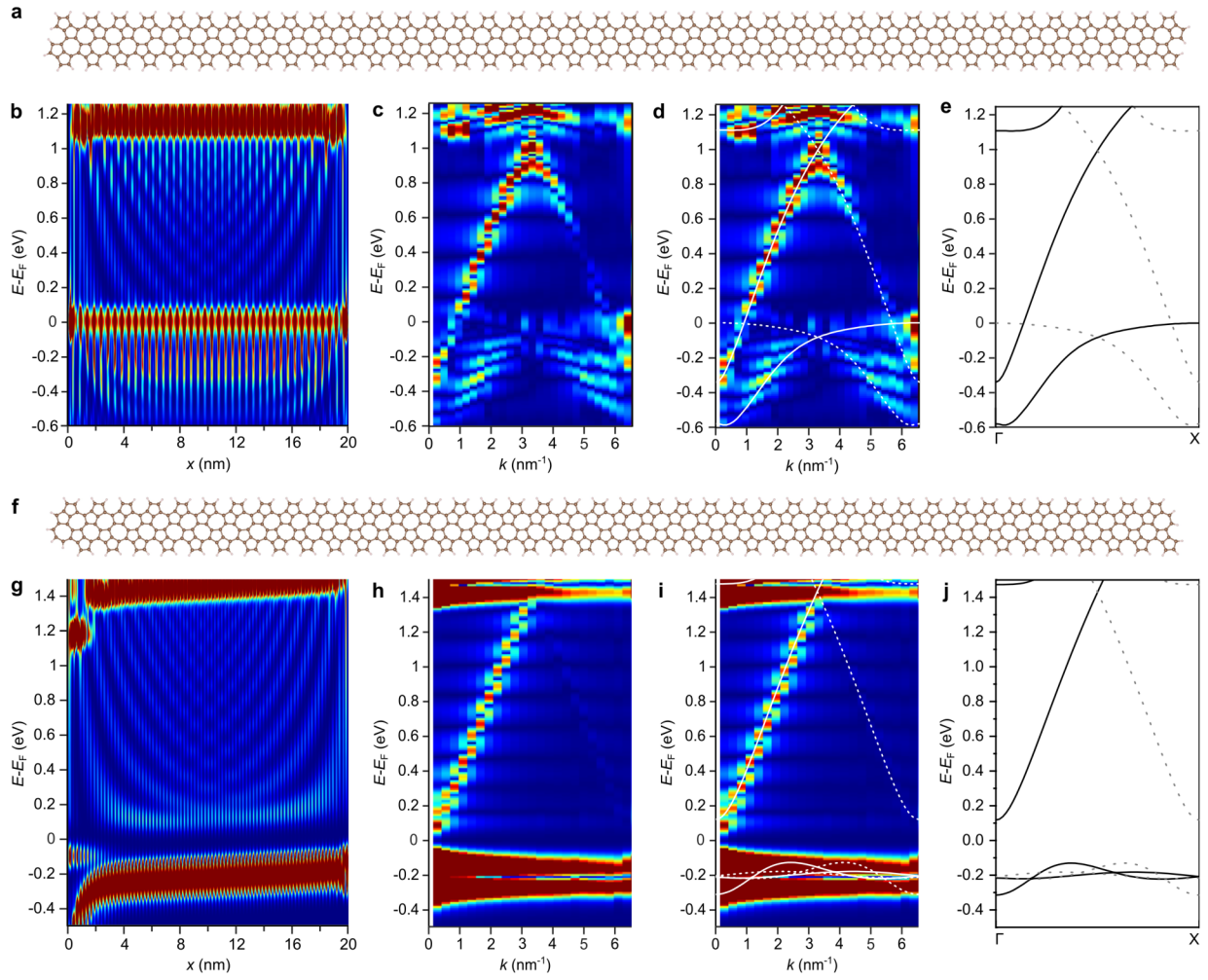
As shown in Supplementary Fig. 25l, comparison of the terminal-sites spectra (in red) with the interior spectra shows that the terminal features are still dominated by the tails of the QWS signals. The interior spectra data set in Supplementary Fig. 25l is replotted from the spectra in Supplementary Fig. 24j of the CPHN **1** (Supplementary Fig. 24g), from the same CPHN **1** segment as in Supplementary Fig. 25a,e. The observed near- E_F QWS-dependent spectral features on the positive-bias side of the terminals on Br/Ag(111) (Supplementary Fig. 25l) are in sharp contrast to the broadening behavior observed in the contact transport data (Fig. 2, Supplementary Fig. 9i,j, and Supplementary Fig. 11f). In addition, the spectra features do not produce any zero-bias peak at ribbon terminals on Ag(111) (Supplementary Fig. 11j,k), which can directly exclude the possibility that the near- E_F peaks in contact transport data (Supplementary Fig. 11f) come from any zero-bias end mode.



Supplementary Fig. 28 | Fitting the experimental and simulated data in FT-LDOS patterns. a–d,

Fitted bands (red curves) using parabolic relation $E(k) = E(k=0) + \frac{\hbar^2}{2m^*} k^2$. The data corresponds to those in Fig. 4g,h,o,p in the main text, respectively. The parabolic fits are restricted to the low- k region near the Γ point, where the effective-mass (quadratic) approximation is valid; at larger momenta the dispersion becomes non-parabolic and is therefore not fitted by a single quadratic form. Owing to the finite lengths of the experimentally measured ribbons, only a limited number of discrete QWS-derived FT-LDOS maxima are available in this low- k region; the fitted effective masses and band-

minimum positions should therefore be regarded as approximate reference values rather than parameters required for the qualitative assignment of metallic or semiconducting band character. The effective masses are obtained from the fits. Error bars indicate the standard deviation (s.d.) of the fitted effective mass and band minimum. **e,f**, Profiles cutting from the patterns at the momenta (k -points) marked by the blue and red arrow in **c,d**, respectively. **g,h**, DFT-calculated bands B₁ and B₂ based on 1D crystal structure of CPHN **1** (**g**) and **2** (**h**), overlaid on the simulated FT-LDOS patterns, the same as in **b,d**, respectively.



Supplementary Fig. 29 | DFT-calculated LDOS maps and FT-LDOS patterns of CPHN 1 and 2 with 40 units. **a,f**, Optimized chemical structures of finite-length CPHN **1** and **2** with 40 repeating units with specific terminal structures. **b,g**, DFT-calculated LDOS maps along the central axis of the optimized structure of CPHN **1** and **2** in **a** and **f**. **c,h**, Calculated FT-LDOSs patterns of CPHNs **1** and CPHN **2** for $0 < k < \frac{\pi}{a}$. Energy broadening applied in all simulations: 50 meV. **d,i**, Calculated FT-LDOSs patterns (the same as **c** and **h**) with overlaid bands from the DFT-calculated band structures in **e** and **j**. **e,j**, DFT-calculated band structures (solid lines) based on freestanding 1D crystals of CPHN **1** (**e**) and **2** (**j**). The dashed lines show the mirrored curves of the band structure during transformation into the FT-LDOS patterns owing to the QPI technique.

Supplementary Section 14. All types of [3]CPHNs show metallic band structures similar to CPHN 1, indicating [3]CPHNs should be metallic independent on the relative orientations of fused PPTLs

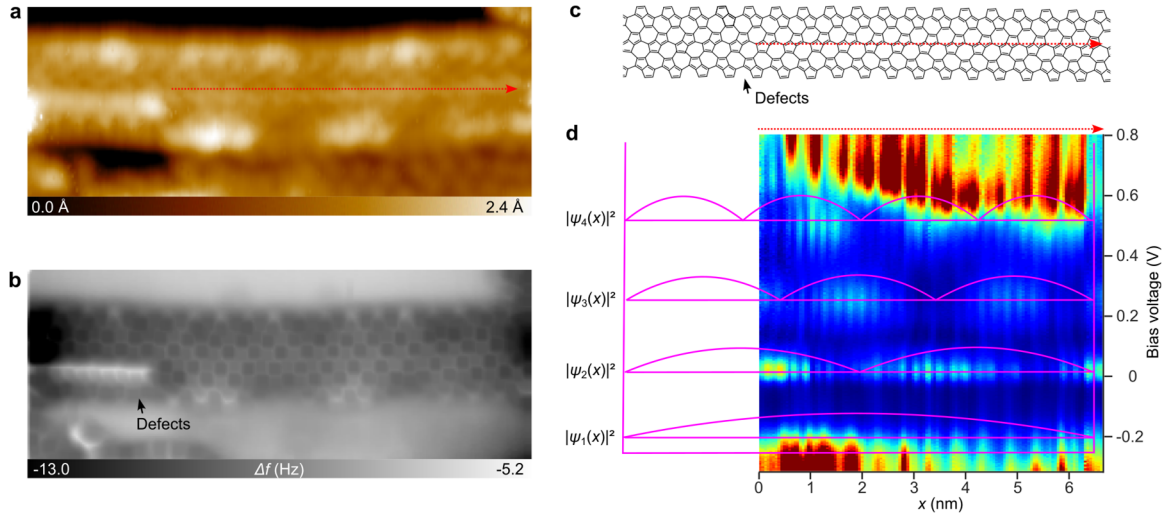
It is interesting to observe that independent on the orientations of the fused PPTLs, all three types of [3]CPHNs with three PPTL widths should be metallic according to the presence of bands B_1 and B_2 around the E_F similar to the ones in CPHN 1 (Extended Data Fig. 10a–f). In all types of [3]CPHNs, nonsymmorphic symmetry breaks down, leading to their property resemble CPHN 1 rather than CPHN 2.

We also characterized the electronic properties of a Br-decoupled [3]CPHN (type 2) composed of three alternately oriented PPTL chains on Br/Ag(111), as evidenced by the STM and nc-AFM images and the derived chemical structures in Extended Data Fig. 10g–j. The experimental 2D-LDOS map (Extended Data Fig. 10k) and FT-LDOS (Extended Data Fig. 10l), recorded along the arrowed line in Extended Data Fig. 10h, reveal a B_1 band (fit shown in Extended Data Fig. 10l) crossing the Fermi level, in agreement with the DFT-calculated band structure in Extended Data Fig. 10e. The corresponding dI/dV maps of the [3]CPHN again display energy-dependent standing waves, as observed for CPHN 1 and CPHN 2, indicating that the B_1 bands in [3]CPHN and in CPHNs 1,2 share the same origin.

Notably, while the 2D-LDOS map in Extended Data Fig. 10k suggests a band minimum near 0.03 V, the dI/dV maps show similar B_1 features even at -0.3 V, implying that the band minimum lies below the Fermi level. This behavior is explained by the extended segment on the left side of the [3]CPHN (Supplementary Fig. 30a–c). The extended length effectively increases the one-dimensional quantum-well size (schematic in Supplementary Fig. 30d), thereby shifting the band minimum below the Fermi level.

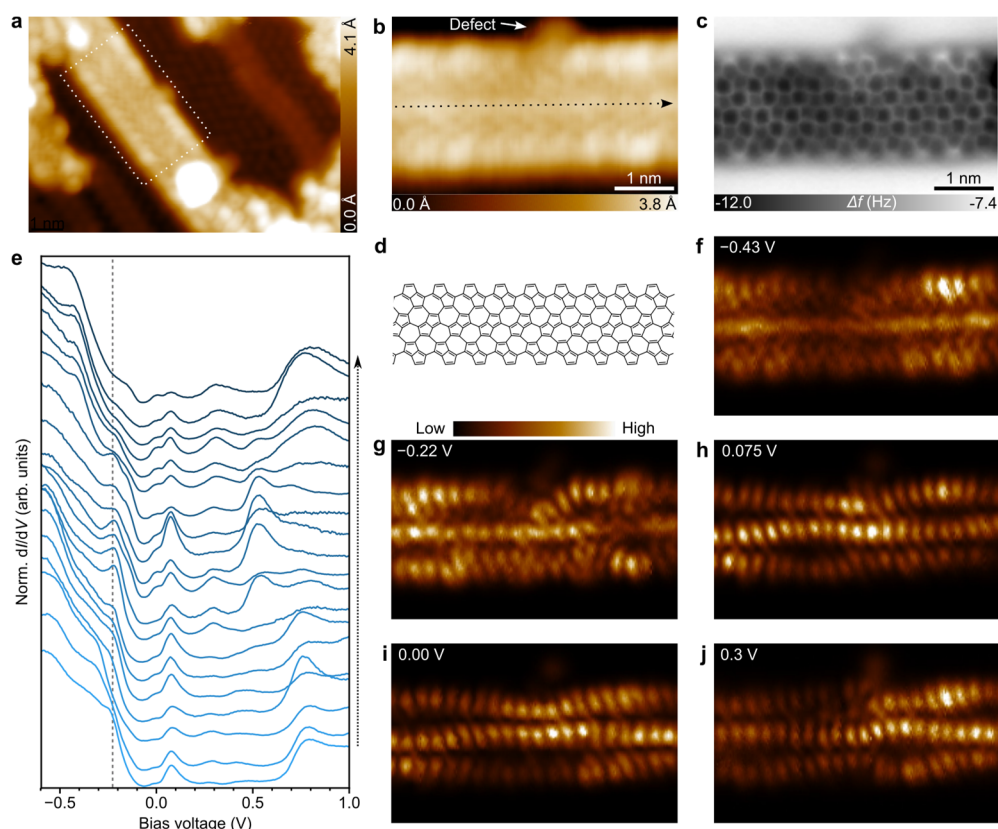
Note that this [3]CPHN (type 2) shows a certain relatively protruded feature near the left end in the STM and AFM images (Supplementary Fig. 30a,b). During measurement, we just recorded the LDOS map within the framed length (Extended Data Fig. 10k) by assuming that the feature could be imperfect [3]CPHN segment within the marked frame. However, after analysing the data, we found that the assumption may not be correct. The protruded feature likely originated from impurities rather than from intrinsic defects in the [3]CPHN itself. This interpretation is supported by our observation that achieving the best fit for the FT-LDOS pattern requires inclusion of the lower-energy signal point (at approximately -0.2 eV, near zero momentum in Extended Data Fig. 10l). Without incorporating this point, the three points above the Fermi level (E_F) cannot be reasonably fitted. By extending the length of the [3]CPHN segment as shown in the STM and AFM images (Supplementary Fig. 30a,b), it can provide a better understanding of the observation by considering that the protruded feature should not affect the potential. When we consider a 1D box model with the extended length of [3]CPHN (Supplementary Fig. 30c), the LDOS map can be interpreted by the 1D quantum well states, as illustrated in Supplementary Fig. 30d. It means that the recorded LDOS map (Extended Data Fig. 10k) is just a partial map of the [3]CPHN, but it seems its FT-LDOS (Extended Data Fig. 10k) can still largely capture the band feature.

Another shorter [3]CPHN (type 2) in Supplementary Fig. 31 provides corroborating signature for metallic behavior. Constant-height dI/dV maps (Supplementary Fig. 31f–j) display pronounced standing waves for sample biases ≥ -0.22 V, implying that the B_1 band minimum lies below the Fermi level. The feature at -0.22 V is also visible in the point spectra (gray dashed line in Supplementary Fig. 31e) and should be the B_1 band minimum, consistent with Extended Data Fig. 10k,l.



Supplementary Fig. 30 | Standing-wave analysis of [3]CPHN composed of three fused PPTLs.

a–c, Enlarged STM (**a**), nc-AFM (**b**), and corresponding derived chemical structure (**c**) of a [3]CPHN (type 2) in Extended Data Fig. 10h. Unlike Extended Data Fig. 10h, the images in **a,b** show an extended length by including the protruded feature in the [3]CPHN segment. **d**, Normalized 2D LDOS map measured along the arrowed grid line in **a** at 128 equidistant points (identical to Extended Data Fig. 10k). The map is overlaid with schematic standing-wave envelopes $|\psi_n(x)|^2$ using a 1D box model with $n = 1, 2, 3 \dots$ denoting the quantum number, where the potential barriers are placed at its possibly true [3]CPHN ends that connect with other species. Tunneling parameters: **a**, -1.0 V, 20 pA; **b**, z -offset = -0.01 nm with respect to STM setpoint of -0.02 V, 20 pA.



Supplementary Fig. 31 | Electronic properties of [3]CPHNs composed of three fused PPTLs.

a–d, Overview (**a**) and Zoom-in (**b**) STM images, nc-AFM (**c**) image and the correspondingly derived chemical structure (**d**) of a section of [3]CPHN adsorbed on Br adlayer on Ag(111) consisting of three fused PPTLs with alternatively altered orientations. **e**, Normalized dI/dV spectra recorded along the arrowed line grids in **b** with equidistant 20 points. The dashed vertical line indicates the shoulder feature in the dI/dV spectra appearing around the middle sites of the [3]CPHN segment. This shoulder feature is similar to the one for CPHN 1 in Extended Data Fig. 7c, hence we can reasonably assign its positions corresponding to the band B_1 minimum for this short [3]CPHN. **f–j**, Constant-height dI/dV maps of the [3]CPHN in **b** recorded at indicated bias voltages. Energy-dependent standing waves were observed like CPHN 1 and 2. All the STM, nc-AFM images and dI/dV maps are recorded with CO-functionalized tips. Tunneling parameters: **a,b**, -1.0 V, 20 pA; **c**, z -offset = 0 nm with respect to STM setpoint of -13 mV, 20 pA. **f–j**, STM setpoint at indicated bias and tunneling current of 500 pA.

Supplementary Section 15. Normalization of dI/dV spectra by the averaged absolute tunnelling current

For the line-grid STS measurements, the absolute intensity of the measured dI/dV spectra can be affected by slow tip-height variations, vertical drift and local changes in the tunnelling junction transparency. These effects introduce a multiplicative intensity factor that can vary from one spatial position to another, producing artificial intensity modulations in stacked dI/dV spectra and 2D LDOS maps. To reduce this contribution and to facilitate comparison of the relative spectral line shapes and QWS peak positions, the displayed dI/dV spectra were normalized by the averaged absolute tunnelling current obtained from the simultaneously recorded $I(V)$ spectra, following a previously introduced averaged-current normalization procedure for grid-mode STS analysis^{13,14}.

For each spectrum recorded at a spatial position $\mathbf{r}$, where $\mathbf{r}$ denotes the position along a line grid or in a grid map, we define the averaged absolute tunnelling current as

$$\langle |I(\mathbf{r}, V)| \rangle_V = \frac{1}{N_V} \sum_{i=1}^{N_V} |I(\mathbf{r}, V_i)|$$

where (N_V) is the number of bias points in the $I(V)$ spectrum. The normalized dI/dV spectrum is then given by

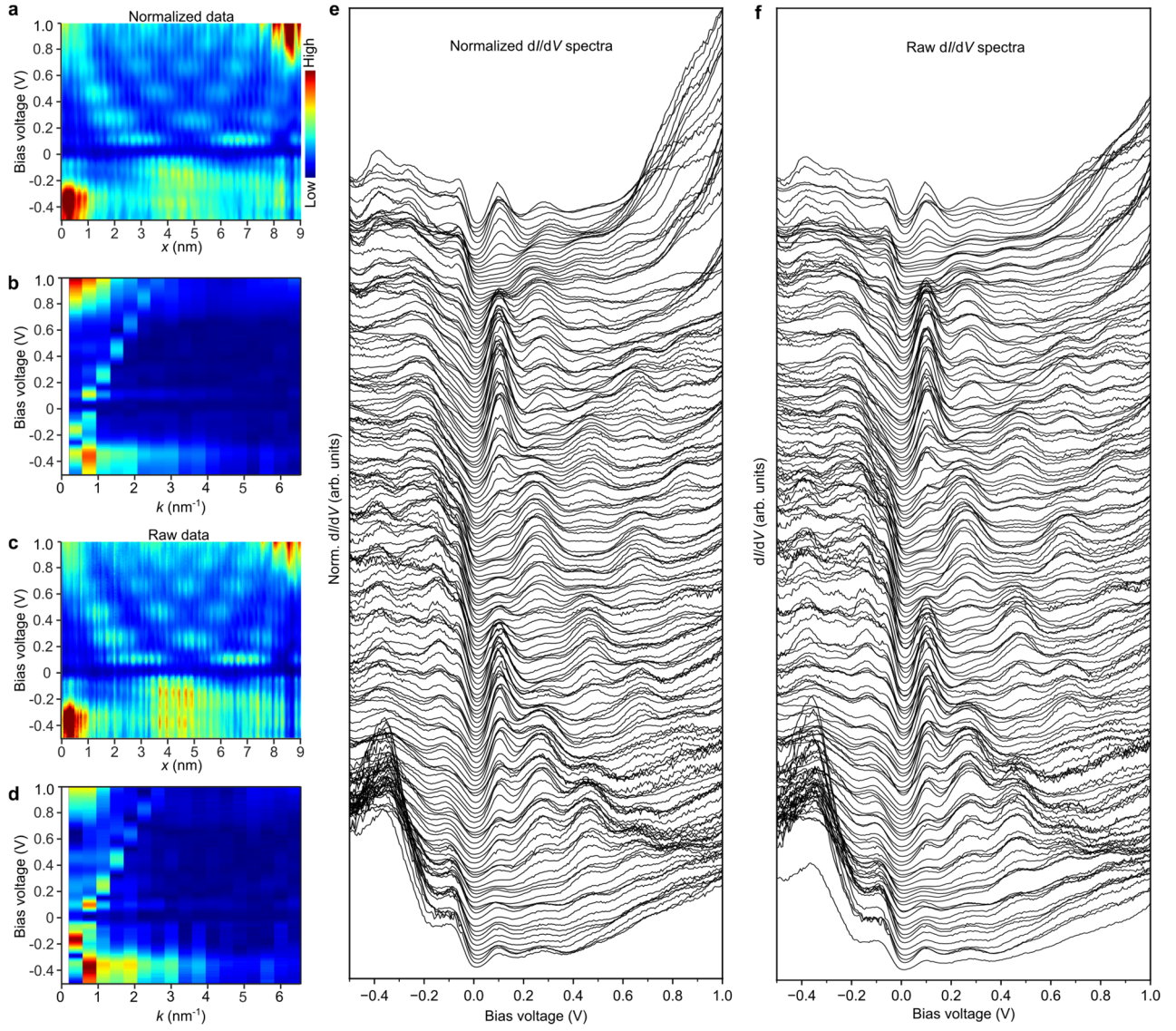
$$g_{norm}(\mathbf{r}, V_i) = \frac{dI/dV(\mathbf{r}, V_i)}{\langle |I(\mathbf{r}, V)| \rangle_V}$$

This normalization uses one scalar factor for each spatially resolved spectrum and therefore preserves the energy positions of all spectral features within that spectrum. It is not intended to provide an absolute LDOS normalization, but only to suppress spatially varying multiplicative intensity factors arising from tip-height fluctuations and junction-transparency variations.

As an example of this normalization, Supplementary Fig. 32 shows the comparison between the normalized data and the raw data. This averaged-current normalization was applied to the displayed STS dI/dV spectra and line-grid datasets for the 2D LDOS and FT-LDOS analyses in Fig. 4e,g,m,o, Extended Data Figs. 7c,d, 8d,k and 10k,l, and Supplementary Figs. 11j,k, 23a,f, 24d–f,j–l, 25c–e,l, 26c,d, 27c,d, 30d and 31e.

To verify that this procedure does not affect the electronic-structure assignment, we compare the normalized and raw line-grid datasets for CPHN 1 in Supplementary Fig. 32. The normalized 2D LDOS and FT-LDOS maps in Supplementary Fig. 32a,b are identical to those shown in Fig. 4e,g, whereas Supplementary Fig. 32c,d show the corresponding maps obtained directly from the raw,

unnormalized line-grid spectra. Comparison of the normalized and raw datasets shows that the normalization changes the relative spectral amplitudes, but does not change the QWS peak positions or the resulting FT-LDOS dispersion. Therefore, the assignment of the B₁-derived QWS manifold crossing E_F is independent of this averaged-current normalization.



Supplementary Fig. 32 | Normalization of dI/dV spectra by the averaged absolute tunnelling current. **a,b**, Experimental 2D LDOS map and corresponding FT-LDOS pattern of CPHN **1**, identical to Fig. 4e,g, respectively. In this dataset, each dI/dV spectrum was normalized by the averaged absolute tunnelling current, $\langle |I(V)| \rangle_V$, obtained from the simultaneously recorded $I(V)$ curve over the same bias range. **c,d**, Experimental 2D LDOS map and corresponding FT-LDOS pattern of the same CPHN **1** dataset plotted from the raw, unnormalized line-grid spectra. **e,f**, Complete dI/dV spectra used to construct the stacked 2D LDOS maps in **a** and **c**, respectively. The spectra are vertically offset for clarity.

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