

Narrow carbon pentaheptite nanoribbon as a covalent metal

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 1:

Reviewer comments:

Referee #1

(Remarks to the Author)

This manuscript investigates carbon pentaheptite nanoribbons (CPHNs) through on-surface synthesis, scanning tunneling microscopy (STM), Synchrotron radiation photoelectron spectroscopy (SRPES), tip-enhanced Raman spectroscopy (TERS), and density functional theory (DFT). The authors engineered a unique on-surface synthesis approach for two isomeric CPHNs, starting with the polymerization of DBCOD precursors on Ag(111), followed by rearrangement and fusion reactions. Nc-AFM and TERS identify the structures of CPHN 1 and CPHN 2 clearly, while SRPES confirms the reaction pathway. They also explored the intrinsic electronic properties of CPHNs on a Br adlayer inserted on the Ag(111) substrate, finding that CPHN 1 is metallic, with VHS states in the dI/dV spectra crossing zero bias, and CPHN 2 is a small-gap semiconductor. The conductance measurements using tip manipulation by lifting the ribbons from the substrate, reveal that CPHN 1 achieves an unexpected conductance of $0.9G_0$, higher than all previously measured graphene nanoribbons and close to metallic single-walled carbon nanotubes.

This study presents a successful synthesis of carbon nanoribbons composed exclusively of pentagons and heptagons, along with the measurement of strong metallic transport in such structures. These results offer new possibilities for designing carbon structures with embedded five- and seven-membered rings, positioning them as key candidates for the semiconductor industry, particularly the interconnects and channel materials. This work introduces novel physics and adds a compelling intersection of chemistry and material science, which will be of great interest to Nature readers. For these reasons, I am supportive of publication in Nature after a few details are addressed.

Comments:

This manuscript presents a thorough investigation of CPHN systems, systematically discussing the synthesis, surface structures, and electronic properties of two distinct CPHNs. The findings demonstrate that CPHN 1 exhibits strong metallicity while CPHN 2 is semiconducting, supported by robust STS and transport data. These results suggest that CPHNs could be promising candidates for semiconductor applications and serve as a new platform for probing materials physics. However, there are a few aspects that could be further developed:

1. Could the origin of the metallicity and small-semiconducting gaps in CPHNs be explored with more detailed theoretical studies? Specifically, which orbitals contribute to the metallic band in CPHN 1, what factors lead to the band opening in CPHN 2, and what is the suitable model to describe their electronic behavior? The current conclusions from the DFT-simulated band structure (Fig. 4a-b, and ED-Fig.6) do not fully clarify the origin of these electronic structures.
2. The TERS data for CPHNs (Fig.3j-k and ED-Fig. 5) does not align closely with theoretical simulations. Could the author explain the reasons for this discrepancy, and the specific new insights provided by the TERS data? The nc-AFM results seem to more effectively support the structural information compared to the TERS data.
3. While discussing the intrinsic properties of CPHNs on the Br adhere layer (Fig. 4c-d, and ED-Fig. 7), it would be more helpful to include the SRPES regarding the Br adhere layer to better support its presence.
4. The manuscript shows the domains of PPTL chains (ED-Fig. 4), however, further clarification of the ratio of the two isomeric CPHNs (Fig. 3a), as well as the yield and limiting factors for the fusion reaction would strengthen the synthesis section. Additionally, a theoretical perspective on factors that limit the width growth in CPHNs (ED-Fig.2c) would be

valuable.

5. For the structures of PPTL (Fig.2) and the wide CPHN (ED-Fig.2c), could the authors investigate their electronic structures and compare the distinctions in electronic behavior associated with varying widths?

6. In the tip-lifting measurements (Fig.4e-i, and ED-Fig.10), have the authors conducted tests with different ribbons? This would mitigate potential influences from extraneous factors, such as materials adhered to the tip (ED-Fig.10a, the top bright region next to CPHN 1), or variations at the opposite ends of the ribbon (ED-Fig.10b)?

7. Finally, the authors need to explain why the contact resistance in the lift-off experiments is surprisingly small. STM break junction experiments routinely suggest that the tip-molecule interface is the limiting constraint on the effective through conductance. The fact that the authors observe values close to G_0 is inconsistent with a large body of work suggesting that the contact resistance for the suggested geometry should limit the conductance to $\sim 10^{-2} G_0$.

Additional minor points for consideration in the main text or SI include:

1. Could the authors clarify the yields for the wet-lab synthesis and provide the carbon NMR spectrums in Supplementary Information Part 1?

2. In ED-Fig.7, are the structures shown PHCN or CPHN?

3. In ED-Fig.8 and 9, it would be useful to include Br/Ag(111) substrate spectra as a reference to identify features in the dI/dV spectra.

It is recommended that the authors address these issues to strengthen the manuscript further. It will be a great contribution to this field.

Referee #2

(Remarks to the Author)

Report on manuscript "Realising narrow carbon pentaheptite nanoribbons with strong metallicity" by Jianmin Huang et al.

This manuscript reports the on-surface synthesis and characterization of so-called pentaheptite nanoribbons, which are highly unusual in the sense that they consist of 5- and 7-membered rings only, in contrast to the well-established 6-membered ring graphene nanoribbons. Interest in such structure derives from early predictions of metallicity in extended, 2D pentaheptite and the prospect of achieving carbon-based nanoscale metallic electrodes and interconnects for replacing (or complementing) traditional metals in devices.

Using a cyclooctadiene precursor, the authors report on an interesting reaction pathway that transforms linear polycyclooctadiene chain into a linear pentalene polymer on a Ag(111) surface under ultrahigh vacuum conditions upon annealing to 400 °C. Further annealing to 500 °C is found to induce the lateral fusion of neighboring polypentalene oligomers, resulting in two different variants of narrow pentaheptite ribbons, which distinguish themselves by the relative orientation of the pentalene units.

The manuscript presents a thorough structural characterization of the pentaheptite ribbons produced in this way. Results from scanning probe methods (STM, nc-AFM with CO-functionalized tip) complemented by DFT-based simulations clearly reveal the 5- and 7-membered ring topology of the ribbons. Vibrational spectroscopy, performed by in-situ tip-enhanced Raman spectroscopy, is somewhat less convincing, because calculated and measured spectra are in relatively poor agreement. The most significant shortcoming of the manuscript, however, is the part aimed at demonstrating "strong metallicity" of one of the two pentaheptite ribbon variants. The authors present both differential conductance scanning tunneling spectroscopy data and two-terminal transport data (from STM tip lift-off experiments), but their discussion of metallicity ultimately relies heavily on a quantitative comparison to DFT calculations, which is problematic, as outlined below.

First of all, DFT (also at the PBE level of theory) is well known to underestimate band gaps. A one-to-one comparison of dI/dV spectra with calculated DOS, on the same energy scale (such as in Fig. 4, or ED Fig. 8 and 9), is not per se meaningful. In particular, the presence of a peak roughly in the energy region where DFT also predicts a peak in the DOS, cannot be taken as evidence that the computed band structure actually describes the situation of the experiment. In Fig. 4, for instance, the computed DOS actually agrees poorly with the experimental dI/dV spectra, which exhibit many more peaks than the DOS.

A proper way of identifying from which bands derive peaks observed in the dI/dV spectra would be via LDOS maps (DFT) and dI/dV maps (experiment). The authors provide this to some extent in Ext. Data Fig. 8 and 9, but the agreement is quite poor. A notable example is the comparison in Fig. 9g vs Fig. 9h, where both maps do show bright maxima but at significantly different spatial locations. Also, the energies chosen for comparison appear somewhat arbitrary, and their choice is not explained.

Given the questionable comparison of experimental data with DFT calculations, the data shown in the manuscript are not sufficient to support the main claim of the manuscript, which is metallicity of the pentaheptite nanoribbons. The authors would rather need to refer to mapping the energy-dependent standing waves formed in finite-length ribbons, which can be Fourier-transformed into reciprocal space to provide the dispersion relation of the underlying band structure. If the ribbons are metallic, one (or several) of the resulting bands will be seen to cross the Fermi energy.

A major drawback of the pentaheptite nanoribbon fabrication via lateral fusion of oligomers is that it is not a deterministic

process that results in atomically precise nanoribbons, but rather in a mixture of differently fused (and non-fused) structures, having different widths, lengths and electronic properties. While this does not compromise the fundamental interest in metallic all-carbon nanoribbons, it clearly prohibits any claims about applicability in devices. The limited quality of the pentaheptite ribbons raises the question whether the yield of the targeted structure(s) can be increased by optimization of the synthesis parameters? Maybe by using a template surface such as Au(110), which may align the chains and potentially enhance the quality of the fused chains?

Overall, given the lack of compelling evidence for the claimed metallicity and the polydispersity of the obtained ribbon products, I cannot recommend publication of this manuscript in Nature. Before submitting to a more specialized journal, I suggest the authors to consider the points outlined below.

1. I am somewhat puzzled by the computed band structures of CPHN 1 and 2 on Br/Ag(111). Considering the significant electronegativity of Br, I am surprised how closely the band structures of CPHNs on Br/Ag(111) resemble those of the gas phase species. This seems to be very different than in the case of Cl/Au(111), which strongly dopes graphene nanoribbons (see ACS Nano 2024, 18, 26, 16622–16631). Is there a good reason for that? BTW, how are the Fermi energies in the calculations defined/set?
2. I am not convinced that the Raman data are fully understood and properly interpreted, and the authors may consider removing this part from the manuscript and devoting a full paper to this aspect. I am concerned by the fact that the most intense peaks in simulations (1315 cm⁻¹ for CPHN 1, 1385 cm⁻¹ for CPHN 2; but also 1072 cm⁻¹ and 895 cm⁻¹, respectively) are absent in experiment. What is the reason for this? Are the calculations missing something important? If not, this discrepancy sheds doubts on the proper structural model for the CPHNs.
3. The experimentally observed zero-bias peak in the CPHN 1 chain (Fig. 4 and Extended Fig. 8), attributed to a van Hove singularity (vHS) by the authors, exhibits an unusually narrow linewidth, which is significantly smaller than a typical DOS singularity. This peak rather reflects the characteristics of an inelastic tunneling process, such as Kondo resonance tunneling, rather than an electronic band structure feature. Have the authors considered that this peak could derive from inelastic tunneling? I am curious whether CPHN 1 may contain spin-polarized states along its edges. I would suggest the authors to perform DFT calculations involving spin polarization, and to compare the outcome with the experimental results. Besides, low-bias step features reminiscent of inelastic electron tunneling are also seen around zero bias with an intensity compatible with the zero bias anomaly (Extended Fig. 8c), again indicating some inelastic tunneling processes via vibrations or spin excitations. Could the authors elaborate on that?
4. Did the author consider finite length effects in the interpretation of their measurements? Judging/guessing from the STM images shown, the STS dI/dV and the contact transport measurements were carried out on short segments with lengths of a few nanometers (less than 10 repeat units?). In this case, one would expect a series of discrete electronic states instead of continuous bands. I therefore recommend performing calculations using finite length ribbon models with effective lengths that match the experiments rather than periodic boundary conditions.
5. Also, larger scale STM images showing the ribbons on which dI/dV were taken should be shown in the Supporting Information (e.g. for the ribbons in Fig. 4).
6. The tip-contact transport results are puzzling. In the case of CPHN 2, the transport measurements show a band shift compared to the STS results, whereas no such shift is observed for CPHN 1. And what accounts for the pronounced broadening of the zero-bias peak, which is an order of magnitude larger than in the STS results? Also, will the end states (are there any?) dominate the transport behavior in such short ribbons? Furthermore, why does the conductance for metallic CPHN 1 and insulating CPHN 2 exhibit almost the same height dependence (slope) in Fig. 4f?
7. As pointed out above, to demonstrate the metallic character of CPHN 1, I suggest that the authors apply one-dimensional quasi-particle interference measurements based on line STS measurement. Compelling evidence would be that the Fourier transform reveals the dispersive bands crossing the Fermi level, as predicted in Fig. 4a.
8. How homogeneous/inhomogeneous is the Br intercalation? Based on Ext. Data Fig. 7a, it appears that segments of PPTL chains are also pushed upward by Br. What is the situation for the CPHN chains? Are they also partially intercalated? If so, what would be the reason?
9. Supplementary Fig. 3 raises questions regarding the dI/dV spectroscopy (or the STM tips used for spectroscopy). The background spectra taken on Ag(111) do not exhibit the typical step-like surface state signal at around -65mV, but rather a peak at positive bias. Interpretation of the spectra acquired with such tip is very difficult.

Referee #3

(Remarks to the Author)

The manuscript (MS) "Realising narrow carbon pentaheptite nanoribbons with strong metallicity" by Huang et al. reports on the on-surface synthesis of carbon nanoribbons composed solely of carbon pentagons and heptagons. The successful synthesis is verified using scanning tunneling microscopy (STM), noncontact atomic force microscopy (ncAFM) and tip-enhanced Raman spectroscopy (TERS). In addition, the authors performed extensive scanning tunneling spectroscopy to investigate the electronic properties of the pentaheptite GNRs and employed density functional theory to corroborate their experimental findings and shine light onto the reaction pathway of the nanoribbon formation.

The MS is mostly well-written, the data are of high quality, the experiments are overall extremely comprehensive, and the conclusions are supported by the data. The MS is very timely as advances in on-surface synthesis have led to a new surge of synthesizing novel carbon allotropes. Pentaheptite had been theoretically predicted around 30 years ago but its realization had remained elusive thus far. In addition to its successful synthesis, the authors demonstrate that a certain form of pentaheptite is metallic (as predicted), which is of note because graphene is semi-metallic and graphene nanoribbons are usually semi-conducting due to quantum confinement. Taking advantage of a skeletal rearrangement during the on-surface synthesis to transform cyclooctadiene into pentalene is another interesting detail, as – to the best of my knowledge – such a

transformation had not been utilized yet for comparable on-surface synthesis pathways. It thus might open a route to the synthesis of other carbon (nano)structures.

Given the topic of the MS and the novelty of the results, this work should be of interest to chemists, physicists and material scientist alike, and I think the manuscript in principle is suitable for publication in Nature. However, there are a few comments I would like the authors to address before I can recommend its publication.

Comments:

Major:

#1: Do the authors have ncAFM images of the PCOD chains? These would be of interest because of two points: (a) It is a bit surprising that Ullmann coupling appears to take place already at RT, because this usually requires slightly elevated temperatures on Ag(111), so it would be interesting to see whether this interpretation is supported by ncAFM images. (b) It would be interesting to see the ncAFM images of the cyclooctadiene, to confirm that they have not yet transformed to pentalene.

#2: Looking at the Fig. 1c, I am wondering if the same pentaheptite nanoribbons could be synthesized using directly a dibromo-pentalene precursor? Did the authors look into that?

#3: The authors state that the lateral growth/fusion would be self-limited, because they observe only rarely nanoribbons made from three PPTL chains. Could this also be due to the coverage or duration of the annealing? If the lateral growth should really be self-limiting, what would be reason for that?

#4: The agreement between the experimental TERS spectra and the calculated Raman modes is not great, both in terms of which modes are observed and their relative intensities. Could the authors please comment on that.

#5 The experimental dI/dV maps in Ext. Data Figs. 8 and 9 are not very homogenous with significant intensity fluctuations along the lobes along the long ribbon axis. This is a bit surprising given that the ncAFM images show that the ribbons are of high quality with seemingly little to no defects. What is the origin of these fluctuations?

#6: Somewhat related to #5: Can the authors exclude other origins of the peak close to zero energy for the CPHN 2 ribbons? E.g., due to magnetism (Kondo effect), in particular because the spectra in Ext. Data Fig. 8c also show some bias-symmetric steps around +/- minus 100 mV, which could also be interpreted as being due to inelastic tunneling processes such as spin flips.

Minor:

#7: Abbreviation PCOD is not defined, I think.

#8: l. 107: Is TTPL a typo and should be PPTL?

#9: Ext. Data Fig. 7: Panel a and b have labels named PHCN. Should those be CPHN?

#10: l. 231 ff.: "[...], and may be beneficial to the suppressed instability caused by the open-shell characteristics that commonly exist in narrow GNRs with pure hexagonal rings." I am not sure whether I understand that statement. Maybe it could be reformulated to make its meaning more clear?

Version 2:

Reviewer comments:

Referee #2

(Remarks to the Author)

Report on MS "Narrow carbon pentaheptite nanoribbons as a covalent metal" by J. Huang et al.

The manuscript by Bing Wang and co-workers reports the on-surface synthesis of carbon pentaheptite nanoribbons (CPHNs). The authors first achieve the formation of polypentalene (PPTL) chains, followed by a lateral fusion process leading to the target CPHNs. Two structural variants are formed, denoted CPHN1 and CPHN2. Both structures consist exclusively of five- and seven-membered rings but differ in the relative orientation of the fused PPTL chains: in CPHN1, the pentalene units of the two PPTL chains have the same orientation, whereas in CPHN2 the orientations are opposite. This structural difference leads to distinct space-group symmetries ($P2/m$ for CPHN1 and nonsymmorphic $Pmc2_1$ for CPHN2) and motivates the electronic distinctions discussed in the manuscript. The theoretical analysis supporting this distinction is twofold. Density functional theory (DFT) calculations demonstrate that CPHN1 exhibits overlapping bands and metallic behaviour, while CPHN2 shows a small bandgap and semiconducting character. The extended SSH tight-binding model introduced in the revised version provides the physical explanation for these DFT results. It identifies how the symmetry imposed by the PPTL orientations controls the allowed inter-chain hopping amplitudes and either lifts the degeneracy at the

X-point (CPHN1, metallic) or enforces a degeneracy leading to flat bands near EF and a finite bandgap (CPHN2). Thus, the reported electronic differences arise from a combination of DFT band-structure modelling and tight-binding symmetry analysis.

The authors further perform tip-contact transport and STM/STS measurements to probe the electronic properties of the CPHNs. Additionally, Br-intercalation is employed to decouple the nanoribbons from the substrate and reveal their intrinsic electronic characteristics. In the revised version of the manuscript, the main modifications include the removal of the poorly matched TERS data, the addition of quasi-one-dimensional QPI measurements (Fourier-transformed dI/dV line profiles), and the use of an extended SSH model to discuss the origin of metallic and insulating properties of the two CPHN variants.

In my opinion, the low quality and yield of the target products remain a major limitation. The synthesis pathway inherently leads to high defect density. The resulting structures display numerous junctions, bending, distortions, and various fusion motifs. The overall sample morphology resembles a disordered two-dimensional network with random connections between PPTL and CPHN segments, rather than well-defined nanoribbons. Only short CPHN segments are found and studied. This strongly restricts reproducibility and systematic investigation.

Compared with the established design of metallic graphene nanoribbons (Science 369, 1597–1603, 2020), the current approach seems significantly more difficult to reproduce or extend. Since the metallic behavior reported here is not an emergent phenomenon but a property relevant for applications, I believe that addressing the present synthetic limitations is essential.

The electronic properties of the synthesized structures also remain insufficiently clarified. In the STS measurements, CPHN1 segments exhibit either insulating or metallic behavior depending on the alignment of the Fermi level with discrete quantum well states. In this situation, the consistent appearance of a robust zero-bias peak in the contact transport measurements is unexpected and requires clearer explanation. Simply omitting this discrepancy from the main figures does not resolve the issue.

Detailed questions/comments:

For sample growth

1. The statistical analysis of the reported 21.8% CPHN yield appears overly simplistic and lacks methodological rigor. As shown in Supplementary Figures 4 and 5, many of the observed products display unclear structures with numerous junctions, bending, distortions, and structural irregularities. Despite this, the authors classify all such defective structures as either CPHN or PPTL, which likely leads to a substantial overestimation of the actual yield.

2. On page 6, lines 19–20, the authors attribute the lower yield of wider CPHNs to “the increased separation of the formed CPHNs from a neighboring PPTL chain (Supplementary Fig. 7a).” However, the experimental observations suggest an alternative explanation. The extensive joint fusions, bending, and distortions within the network likely suppress the lateral mobility of all nanoribbons, thereby reducing the yield of wider fused structures. Moreover, the theoretical calculations used to support the proposed mechanism rely on idealized, isolated, straight ribbon models, which do not reflect the structural disorder observed experimentally. I note that Reviewer 3 already raised this issue in the first round (comment #3), and it remains unresolved.

For electronic properties

3. My main concern is the discrepancy between the QPI and contact transport measurements for CPHNs. The QPI patterns clearly reveal quantization of the dispersive band, with 0.1–0.2 eV gaps between discrete levels depending on ribbon length. This indicates that the metallic or insulating behavior of short CPHN ribbons depends on whether the Fermi level aligns with a discrete energy level or falls within a gap, both of which are observed in the STS data (ED-Fig. 7 and ED-Fig. 9). In contrast, the contact transport measurements for CPHN1 consistently exhibit a strong zero-bias peak. Given that the authors employ an extended SSH model, the question arises whether this zero-bias anomaly could originate from a topological end mode or another mechanism intrinsic to the model. An alternative explanation that should be considered is the pinning of one of the discrete quantum well states, plausibly the first valence or conduction band state, to the Fermi level of the tip or sample, which could also give rise to a robust zero-bias feature. This requires clarification.

Beyond this conceptual discrepancy, there are further issues with the LDOS patterns and their Fourier transforms. The experimental QPI dataset is very limited: across the main text, Extended Data, and Supplementary Information, the LDOS patterns and FT-dI/dV line profiles appear to be essentially the same data as in Fig. 4e (CPHN1) and Fig. 4m (CPHN2), without additional independent measurements. The STM and AFM images of the ribbon segments used for the LDOS line profiles never show the actual termini of the ribbons, although these termini are crucial for the formation of standing waves. The data should cover the full ribbon length and clearly indicate the positions where dI/dV spectra were recorded. In addition, the parabolic fitting of the FT-LDOS patterns, for example in Supplementary Fig. 19, is performed only over the first few low-energy points. Either the fit should be carried out over the full accessible energy range, or the authors should justify why it is restricted to small energies. Finally, the agreement between experimental and computed LDOS maps in Fig. 4m,n is rather poor in terms of the positions of the intensity maxima, whereas the corresponding Fourier-transformed maps in Fig. 4o,p look surprisingly similar. The authors should explain how good agreement is obtained in Fourier space despite visible discrepancies in real space.

4. It remains unclear how short, finite ribbons with discrete energy levels could support electron mobilities comparable to those of carbon nanotubes. The manuscript should address this point.

5. There is a typo in the caption of Extended Data Figure 6 (“Sin-unpolarized”).

6. The statement “The simulated results highly reproduce the experimental observations (Extended Data Fig. 8), providing further confirmation of the metallic and semiconducting nature of CPHN-1 and CPHN-2 in their finite lengths” is not scientifically rigorous. Whether a finite system exhibits metallic or insulating behavior depends on the Fermi-level alignment relative to the discrete quantized levels. Even an intrinsically metallic ribbon can appear insulating at finite length. If the authors intend to discuss the infinite-length limit, they should state this explicitly and revise the discussion accordingly.

7. The criteria used to determine energy gaps from transport measurements are not clearly defined. It is unclear how the values of 0.24 eV (CPHN2, ED-Fig. 4) and 50 meV (PPTL, Supplementary Fig. 10) are obtained. In addition, the reliability of transport measurements on very short nanoribbon segments—as shown in ED-Fig. 4b and Supplementary Figs. 9e and 9f—needs to be evaluated, since end states or defects may dominate the observed behaviour.

8. In the tight-binding model, the positions and physical meaning of the a, b, and c sites within a single unit cell are not clearly described. Showing the corresponding atomic orbitals would significantly improve the clarity of the model.

Regarding the authors' reply and other reviewers' comments

9. All three reviewers noted that the TERS data do not align with the calculations. The authors attribute this discrepancy to surface adsorption, but the strong structural disorder and frequent joint fusions likely play a more significant role. The authors should examine the reproducibility of the Raman spectra to rule out large variations caused by structural defects, which may also affect the electronic properties.

10. As noted by Reviewer 2, the yields of CPHNs remain low. The authors claim improved yield, but the supporting statistical analysis is still insufficient. The sample quality shown in the revised submission remains poor.

11. The authors' reply regarding the zero-bias peak in CPHN1 is not convincing. The peak appears consistently across all transport measurements, which contradicts the claim that it arises only when the metallic band minimum accidentally aligns with the Fermi level. Presenting conductance over a larger bias range would help determine whether quantum well states are present and clarify the origin of the zero-bias anomaly.

In conclusion, the study addresses an interesting novel type of nanoribbon, but in my view the current version does not yet provide the structural control, data completeness, and electronic characterization required to support the central claims. I would encourage the authors to revisit these points comprehensively.

Referee #3

(Remarks to the Author)

This is the review for the revised version of the manuscript (MS) “Realising narrow carbon pentaheptite nanoribbons with strong metallicity” by Huang et al.

All my comments have been replied to in satisfactory manner. The authors have included additional experimental and theoretical data which significantly improved the MS and made it more convincing. In my opinion, also the issues raised by the other reviewers have been addressed well (there were several similar/closely related comments between reviewers).

I have only two final minor comments (see below) and recommend publication of the MS in Nature.

Minor comments:

#1: In their reply to my comment #6, the authors write that the conductance peak around zero bias should not be assigned to a vHS. But in the revised version of the MS, they write on p. 12, l. 18f, that “The high DOS near the E_F can be attributed to contributions from the van Hove singularity (VHS) states of band B-2 [...]” Either I am misunderstanding this sentence or it contradicts the authors' statement from their reply. Please comment/correct/reformulate.

#2: In Extended Data Fig.9 i,j the labels on the y axis read “Bias voltage (V)”. Should this maybe be “ $E-E_F$ (eV)”, as in panels f and g?

Referee #4

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports.

Version 3:

Reviewer comments:

(Remarks to the Author)

General assessment

I appreciate the effort the authors have made to revise the manuscript and to address several of the previously raised points. However, after carefully examining both the revised version and the rebuttal, I remain unconvinced that the central claims are sufficiently supported. My concerns relate to the structural quality and yield of the material, the rigor and internal consistency of the electronic data interpretation, and the actual level of advance relative to prior work.

A recurring issue throughout the manuscript is that the interpretation appears to be guided by the intended conclusion, namely the claim of intrinsic metallicity, rather than being strictly derived from the experimental observations. Several key arguments rely on selective interpretation of the data, while alternative explanations are not rigorously considered or excluded. In its present form, the work is interesting and may be suitable for a more specialized journal, but it does not reach the level of clarity, rigor, and unambiguous evidence expected for publication in Nature.

Structural quality and statistical analysis

The most serious concern is the discrepancy between the structural quality evident in the STM images and the reported statistical yield. The statistical analysis remains unconvincing. Many segments classified as target CPHN ribbons are clearly defective, bent, or involved in junctions, and therefore cannot reasonably be considered well-defined nanoribbons. This becomes particularly evident when inspecting the marked "target ribbons" (yellow segments), where a significant fraction is structurally imperfect, short, or part of fused networks. In the attached PNG, I have indicated several such examples (red circles) where the assignment appears questionable.

The counting procedure, based on pentalene units and area normalization, does not reflect the actual usability of the structures for electronic characterization and effectively inflates the yield by including structurally ambiguous or defective motifs. A truly defect-free segment should be straight, isolated, and sufficiently long, on the order of at least ten repeat units, yet such segments appear to be rare in each presented scan frame. Consequently, the reported yield does not correspond to the yield of physically meaningful nanoribbons, which undermines both the statistical analysis and the reliability of the subsequent electronic measurements.

Relation to prior work

The conceptual advance relative to prior work is not convincingly established. Carbon chains containing 5/7-membered carbon rings have already been reported in earlier studies (JACS 2019, 141, 44, 17713–17720; JACS 2020, 142, 23, 10291–10296), where the concept of lateral fusion employed in the present manuscript is essentially the same as that introduced in the 2019 work. Importantly, the principal limitation of this approach, namely the low yield of the target structures, remains unresolved here.

With respect to electronic properties, the manuscript does not convincingly establish a substantive advance beyond the metallic graphene nanoribbons reported in Science 369, 1597–1603 (2020). In fact, the present system appears significantly more difficult to control, while not providing a clearly superior or fundamentally new electronic functionality.

Electronic structure and dispersion analysis

The analysis of the electronic structure raises several concerns. The extraction of a parabolic dispersion and the associated fitting appear misleading. Based on the presented data, the dispersion seems to originate from the Fermi level rather than from approximately -0.15 eV as drawn in the manuscript, and the fitting is restricted to a limited energy range without clear justification. This weakens the reliability of the extracted band parameters.

A particularly striking example is SI Fig. 24d, where a parabola is fitted to three (3) data points. This does not make sense. More generally, the manuscript does not treat the distinction between finite-size quantization and intrinsic metallicity in a sufficiently rigorous manner. The experimental data clearly show discrete quantum well states and energy gaps that depend on ribbon length and local environment. In addition, all spatially resolved STS maps for CPHN1 show a relatively homogeneous gap-like feature around the Fermi level, which appears fundamentally different from the higher-energy quantized gaps. No explanation is provided for this observation, and it is not clear how this behavior is consistent with a simple metallic band crossing the Fermi level.

Zero-bias peak and Fermi-level pinning

The explanation of the robust zero-bias peak in transport measurements remains unconvincing. I initially considered whether this feature could originate from Fermi-level pinning, as suggested by the authors. However, based on the calculations shown in Supplementary Fig. 18, there is no clear evidence supporting such an interpretation. The quantum well states appear to shift systematically with increasing ribbon length rather than exhibiting a distinct state pinned at the Fermi level.

Given that the zero-bias peak is observed consistently across different junctions, an explanation based on Fermi-level pinning requires stronger and more direct support than currently provided.

Unresolved spectral features

Another unresolved issue is the presence of a gap-like feature near the Fermi level in several datasets, including Fig. 4e, Supplementary Fig. 23c, and Supplementary Fig. 24c. This feature is clearly distinct from the larger quantized gaps observed at higher energies and appears consistently across different measurements. Its origin is not explained and appears incompatible with the interpretation of a simple metallic band.

In addition, the spectra shown in Supplementary Fig. 23e exhibit pronounced asymmetric, Fano-like line shapes together with position-dependent broadening. Similar broadening behavior is also observed in the contact transport data (Supplementary Fig. 9i and j). It is unclear how these features should be understood. In particular, it would be important to clarify whether such asymmetric line shapes are also present in background spectra and whether they reflect intrinsic

properties or measurement-related effects.

Band-edge assignment and internal consistency

There are also inconsistencies in the assignment of band edges. The authors consistently assign the energy range around -0.1 to -0.2 eV as the onset of the conduction band for CPHN1 (for example in Supplementary Fig. 23d and Fig. 24d), but this assignment does not appear to be clearly justified by the presented data. Moreover, applying the same assignment procedure to Supplementary Fig. 25d would lead to the conclusion that CPHN2 is metallic, which contradicts the authors' own interpretation. This indicates a lack of internal consistency in the analysis.

Additional experimental requirements

To clarify the electronic structure, it would be important to provide STS spectra over a wider energy range, extending down to approximately -1.0 eV for the intercalated CPHNs, in order to verify that the gap positions are indeed around -0.8 eV and -0.6 eV for CPHN1 and CPHN2, respectively. In addition, more direct and systematic evidence is needed to support the proposed Fermi-level pinning mechanism, for example through comparative measurements under different junction conditions.

Conclusion

While the system under study is interesting and the experimental effort is evident, the manuscript does not yet provide sufficiently controlled structures, rigorous statistical analysis, or internally consistent electronic interpretation to support its central claims. In particular, the conclusion of intrinsic metallicity is not convincingly demonstrated. I therefore cannot recommend publication in Nature.

Referee #3

(Remarks to the Author)

This is the review for the latest version of the MS "Narrow carbon pentaheptite nanoribbon as a covalent metal". I was satisfied with the previous revision of the MS, which in my opinion convincingly demonstrates the synthesis of a novel family of GNRs, using a very surprising and interesting synthesis route. Even though the yield is not very high and there is room for improvement in terms of sample quality, to me it seems sufficient to claim that the synthesis pathway works in principle (given that the AFM images Fig. 2c,e shows defect-free segments of 20+ unit cells) and to assess the basic bulk electronic properties of the GNRs.

The experimental line spectra and their FFTs in my opinion show convincingly that for CPHN1 the CB-derived quantum well states in finite segments span across the Fermi level, while they remain above Fermi for CPHN2, indicating that the former should be intrinsically metallic in the limit of very long/infinite ribbons. While the spectra are not perfect and there might be additional features that cannot be assigned with complete certainty, this metallicity would correspond to the predicted behaviour and the FFTs fit well with the authors' simulations.

I have also seen the new set of comments from reviewers #2 and #4 and was asked to briefly comment on them as well.

Structural quality and statistical analysis: I agree that there is room for improvement in terms of quality and yield of the synthesized ribbons. In particular high-profile publications of novel GNRs mostly demonstrate significantly better yield and structural quality. However, once one broadens the scope a bit and looks at recent high-impact studies of other carbon nanostructures by on-surface synthesis, the results in the current MS are in line with other publications in the field. E.g., the first publication on the OSS of cyclocarbon (Science 2019) had a yield of less than 20%, if I remember correctly. Some recent high-profile publications of 2D networks based on carbon nanostructures showed only a few defect-free unit cells with low long-range structural coherence (this statement is not meant as a criticism of said papers), see e.g., Science 384, 895 (2024).

Relation to prior work: I agree that lateral fusion is well-established. However, taking advantage of on-surface skeletal rearrangement to produce purely 5-7 ribbons is novel, and taking the AFM images in Fig. 2, the resulting ribbons seem to be longer and of higher structural quality than those in the two JACS papers. It is true that one could argue that in terms of metallicity, these new ribbons do not constitute a substantive advancement compared to the 2020 Science paper. However, the current MS does demonstrate a very different mechanism to introduce metallicity, and in my personal opinion, is not less convincing (if not more) than the aforementioned Science paper.

Electronic structure and dispersion analysis: I agree that fitting a parabola to three points is not optimal, but in my opinion the simulations show convincingly that the quadratic approximation is valid only for low k -values. I also see the exact values derived from the fits of only minor importance to the MS and its main conclusions. Regarding the distinction between metallicity in the infinite limit and semiconducting due to quantum confinement in finite segments, I do think the manuscript has significantly improved since the first version, but this distinction could indeed be further emphasized.

Zero-bias peak and Fermi-level pinning: I agree with reviewers 2 and 4 here. The simulations do not really show Fermi level pinning and do not seem to explain well the observed broad peaks around zero bias in the transport measurements. But in my opinion the set-up of the calculations also does not really mimic the experiments. Maybe instead of changing the length of the ribbon, the authors could try a simulation where the ribbon length is constant, but the amount of overlap of the ribbon with one of the leads is changed? This should be a better approximation to the experimental set-up, I would think.

Unresolved spectral features: To me, the appearance of the discretization gap is in line with previous publications, see e.g., Nat. Comms. 16, 5632 (2025). The features in SFig. 23e look like electronic states in a mixed-valence regime (maybe related to localized states at the non-perfect ribbon termini), which typically give rise to asymmetric orbital-like features in dI/dV close to/at zero bias, see e.g., Science 309, 1542 (2005) and Nanotechnology 19, 065401 (2008).

Band-edge assignment and internal consistency: Here I think I disagree with the reviewers. If I was given just the experimental dI/dV line spectra and their FFTs and nothing else; no theory, no predictions, I would make the same qualitative assignment regarding the position of the conduction bands (crossing Fermi vs not crossing Fermi) as the authors. Given the dispersion of the quantized states and the distribution of their lobes, this seems to me the most sensible interpretation. The data are not perfect, there might be additional features that are not fully understood, especially related to additional states localized at the defective ribbon ends, but to me that does not necessarily invalidate the characterization of the bulk electronic properties based on the line spectra above the ribbon interior.

Referee #4

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports.

Version 4:

Reviewer comments:

Referee #3

(Remarks to the Author)

This is the review for the revised version of the manuscript "Narrow carbon pentaheptite nanoribbon as a covalent metal" by Huang and co-workers.

The authors refined the statistical analysis of the synthesis yield, did another set of transport calculations to investigate the origin of the broad zero-bias feature in the lifting experiments, and modified the text to put the manuscript into context of related works and to add some qualifiers and clarify some of the interpretations, thereby addressing all the points raised in the previous round of reviews. The main results are unaffected by these changes, and as I stated in my previous report, I find the conclusions regarding the crossing of the Fermi energy by the CB and thus the metallicity convincing, as well as the new revisions.

This being said, having seen Fig. R1 and new Fig. S19, I do have two final comments:

#1: In Fig. R1, panel d shows the wave functions of the QWS around the Fermi energy for a finite metallic (in the infinite limit) ribbon. Based on their shape and symmetry, bands 660 to 656 clearly belong to the same, upward dispersing band, which seems to be crossing Fermi. However, I am quite puzzled by bands 655 to 653, which – based on their shape and symmetry – seem to form a distinct set of QWS derived from a downward dispersing band. Do the authors have any insights on the nature or origin of these states? If they arise from the VB, then would that suggest some kind of band inversion?

#2: The authors made another set of transport calculations, Fig. S19, based on a comment of mine in my previous report, and I very much appreciate the authors efforts. However, I think there was a misunderstanding about my idea. In their new calculations, the authors still change the total length of the ribbon, such that even though the overlap of one ribbon end with the lead increases, the length of the free-standing segment stays the same.

My idea was to keep the total length constant but change the amount of overlap of one of the ends with its lead, such that the free-standing segment gets longer while segment coupled to the lead get shorter. That is my somewhat naïve experimentalist idea of how the calculations would best mimic the experiment, where I-Vs are measured while the ribbon is step-by-step delaminated from the surface by the tip. But I have to admit that I have no idea if that would yield anymore insights than the previous calculations. I also do not know how expensive these kind of calculations are, and I am in principle fine with that feature being tentatively assigned to "possible contact-induced level/resonance alignment" (as to me, a lack of definitive explanation of that feature does not weaken the conclusions made based on the dispersion of the CB-derived QWSs).

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Referee #1 (Remarks to the Author):

This manuscript investigates carbon pentaheptite nanoribbons (CPHNs) through on-surface synthesis, scanning tunneling microscopy (STM), Synchrotron radiation photoelectron spectroscopy (SRPES), tip-enhanced Raman spectroscopy (TERS), and density functional theory (DFT). The authors engineered a unique on-surface synthesis approach for two isomeric CPHNs, starting with the polymerization of DBCOD precursors on Ag(111), followed by rearrangement and fusion reactions. Nc-AFM and TERS identify the structures of CPHN 1 and CPHN 2 clearly, while SRPES confirms the reaction pathway. They also explored the intrinsic electronic properties of CPHNs on a Br adlayer inserted on the Ag(111) substrate, finding that CPHN 1 is metallic, with VHS states in the dI/dV spectra crossing zero bias, and CPHN 2 is a small-gap semiconductor. The conductance measurements using tip manipulation by lifting the ribbons from the substrate reveal that CPHN 1 achieves an unexpected conductance of $0.9G_0$, higher than all previously measured graphene nanoribbons and close to metallic single-walled carbon nanotubes.

This study presents a successful synthesis of carbon nanoribbons composed exclusively of pentagons and heptagons, along with the measurement of strong metallic transport in such structures. These results offer new possibilities for designing carbon structures with embedded five- and seven-membered rings, positioning them as key candidates for the semiconductor industry, particularly the interconnects and channel materials. This work introduces novel physics and adds a compelling intersection of chemistry and material science, which will be of great interest to Nature readers. For these reasons, I am supportive of publication in Nature after a few details are addressed.

[Reply: We thank the Reviewer's appreciation of our work and support its publication in Nature.](#)

Comments:

This manuscript presents a thorough investigation of CPHN systems, systematically discussing the synthesis, surface structures, and electronic properties of two distinct CPHNs. The findings demonstrate that CPHN 1 exhibits strong metallicity while CPHN 2 is semiconducting, supported by robust STS and transport data. These results suggest that CPHNs could be promising candidates for semiconductor applications and serve as a new platform for probing materials physics. However, there are a few aspects that could be further developed:

1. Could the origin of the metallicity and small-semiconducting gaps in CPHNs be explored with more detailed theoretical studies? Specifically, which orbitals contribute to the metallic band in CPHN 1, what factors lead to the band opening in CPHN 2, and what is the suitable model to describe their electronic behavior? The current conclusions from the DFT-simulated band structure (Fig. 4a-b, and ED-Fig.6) do not fully clarify the origin of these electronic structures.

Reply: We are grateful to the Reviewer for these insightful suggestions.

We have performed additional theoretical studies to address the comments. In the revision, we rewrite the section in subtitle of “Calculated electronic band structures”, by including both DFT and TB calculations. The results are presented in **Fig. 3**, **Extended Data Figs. 5,6**, and **Supplementary Figs. 11-14**. The details of theoretical modelling and analysis are also given in **Supplementary Section 7 and 8**.

Here, we briefly summarize some important theoretical modelling issues and conclusions.

1. Spin-unpolarized and spin-polarized calculations.

We performed both spin-unpolarized and spin-polarized DFT calculations with PBE and HSE 06 functionals for freestanding CPHN **1** and **2**, and CPHN **1** and **2** on Ag(111) and on Br/Ag(111) substrates (**Fig. 4**, **Extended Data Figs. 5, 6**, and detailed analysis in **Supplementary Figs. 11-14**). For comparison, freestanding planar PPTL are also calculated (**Fig. 3a**, **Supplementary Fig. 12**). Basically, the results from spin-unpolarized and spin-polarized DFT calculations are consistent. Particularly, for CPHN **2**, the spin-unpolarized and spin-polarized DFT calculations give nearly the same results, showing no magnetic property in CPHN **2** (**Fig. 3**, **Supplementary Fig. 11**). While there is spin splitting in the band structure of CPHN **1** obtained in calculations including spin polarization (**Extended Data Fig. 5**), the magnetism turns out to be quite fragile. It is observed that the magnetic moment has been quenched under a slight doping level of 0.1 electrons. It suggests that the results from spin-unpolarized DFT calculations can be well used to describe the band structure of CPHN **1** and **2**. Hence, we present the results from spin-unpolarized DFT calculations (**Fig. 3**), compared with the spin-polarized results (**Extended Data Fig. 5**).

2. Tight-binding calculations.

To gain insight into the electronic properties of CPHN **1** and **2**, we also performed tight-binding (TB) calculation by adopting an extended Su–Schrieffer–Heeger (SSH) model for PPTL, and an extended SSH ladder model for CPHN **1** and **2** (**Fig. 3, Methods, Supplementary Figs. 12-14, and Supplementary Section 8**). Three lattice sites per repeating unit are considered in PPTL, and CPHN **1** and **2** are modeled by two coupled PPTLs with different symmetries. Our symmetry analysis shows that CPHN **2** possesses a nonsymmorphic symmetry, which leads to the symmetry-protected Dirac-like points at the X point of the Brillouin zone. This degeneracy has been confirmed by both the DFT and TB calculations. However, there is no enforced degeneracy in CPHN **1** at the X point. TB calculations show that the originally localized states at the middle C-C bond of each pentalene in PPTL contribute to the nearly flat band close to the E_F . In CPHN **2**, the suppressed inter-chain hopping between these sites of two PPTLs also contribute to the formation of two flat bands close to the E_F , leading to its semiconducting behavior. Instead, in CPHN **1**, the enhanced inter-chain hopping between these sites with localized states, in particular the hopping amplitude reaching to -0.766 eV between the next-nearest neighbor sites of two PPTLs, contribute to the band overlap because of the degeneracy lift at the X point, predominantly leading to the observed metallic bands in CPHN **1**.

These additional calculations and analysis have put our conclusions on the solid ground. Moreover, these calculated band structures have also been confirmed by our experimental results, such as the QPI experiments and their simulations (**Fig. 4, Extended Data Figs. 8,9, and Supplementary Figs. 19,20**).

2. The TERS data for CPHNs (Fig.3j-k and ED-Fig. 5) does not align closely with theoretical simulations. Could the author explain the reasons for this discrepancy, and the specific new insights provided by the TERS data? The nc-AFM results seem to more effectively support the structural information compared to the TERS data.

Reply: We agree with the Reviewer that the nc-AFM results already provide clear structural information. The original purpose of measuring the TERS data was to highlight the differences in vibrational modes between pure odd-membered ring CPHNs and GNRs composed entirely of hexagons. We also thank the Reviewer for pointing out that the current TERS data does not align well with theoretical simulations. This discrepancy could be primarily ascribed to the adsorption of CPHNs on the Ag(111) surface and the enhancement of the plasmon Pico cavity, while the vibration modes are calculated based on free-standing CPHNs. Considering the complexity of the physics therein, we removed the TERS part from

the former version into a separate study as also suggested by Referee 2.

One of the most important factors cause the discrepancies is that the vibration modes are mainly in-plane, but the normal TERS measurements is not sensitive to the in-plane modes. While we have performed measurements using contact-mode TERS, the complexity in the contact-mode TERS still exists. To share our current progress at this point, we have performed additional calculations by including the Ag(111) substrate and the plasmon field of the Pico cavity. The newly calculated TERS spectra are shown in **Fig. R1** below, better agreement has been achieved when compared to the experimental TERS spectra. We find that the peak at 760 cm^{-1} can be acted as a fingerprint to distinguish the two types of CPHNs, where this peak is absent in CPHN **1**.

The simulated vibrational mode at 621 cm^{-1} (corresponding to the experimental mode of 644 cm^{-1}) in CPHN **1** (**Fig. R1c**) exhibits strong Raman intensity at the ribbon edges but is markedly weaker at the inner sites adjacent to the outer pentagon. This spatial dependence mirrors the experimental Raman spectra (**Fig. R1a**), where the 644 cm^{-1} peak diminishes from edge to center. By contrast, the 642 cm^{-1} mode in CPHN **2** (**Fig. R1d**) shows no discernible spatial variation, consistent with the uniform Raman peak at 650 cm^{-1} (**Fig. R1a**). Distinct differences also emerge at higher frequencies: in CPHN **1**, coupled vibrations of the two PPTL chains give rise to modes at 829 and 835 cm^{-1} , matching the experimental peak at 823 cm^{-1} recorded at the ribbon center. In CPHN **2**, however, a 762 cm^{-1} mode corresponding to nearly independent chain vibrations is observed, with rather weak central intensity reflecting reduced interchain coupling, in agreement with the SSH ladder tight-binding model. Notably, CPHN **1** supports only a Raman-inactive interchain mode at 771 cm^{-1} in the $700\text{--}800\text{ cm}^{-1}$ range, explaining the absence of experimental features there. Thus, the 762 cm^{-1} mode serves as a fingerprint of CPHN **2**, absent in CPHN **1** owing to its stronger interchain coupling. Even though, the peak-to-peak agreement between the experimental and calculated results is still insufficient. Fortunately, the AFM images have already provided sufficient clear distinguishment by their structures between CPHN **1** and **2**.

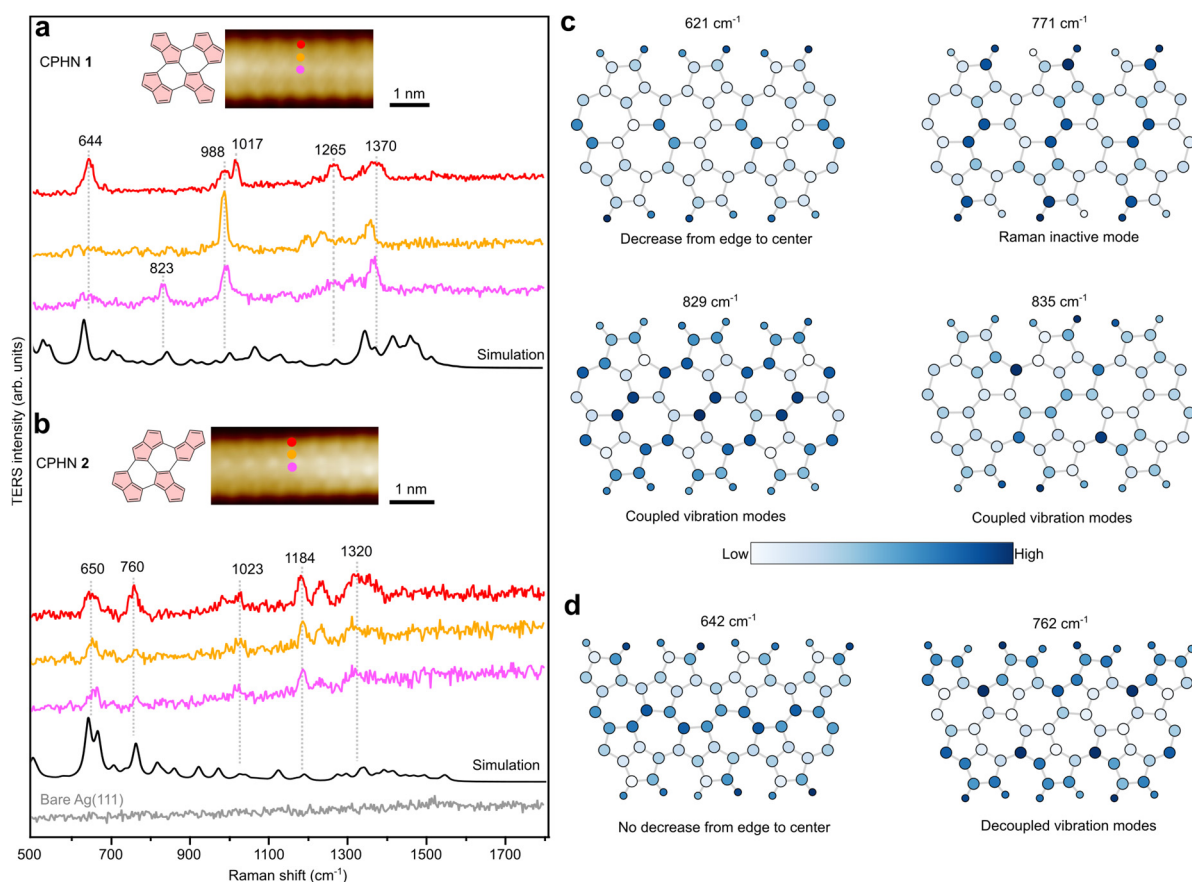


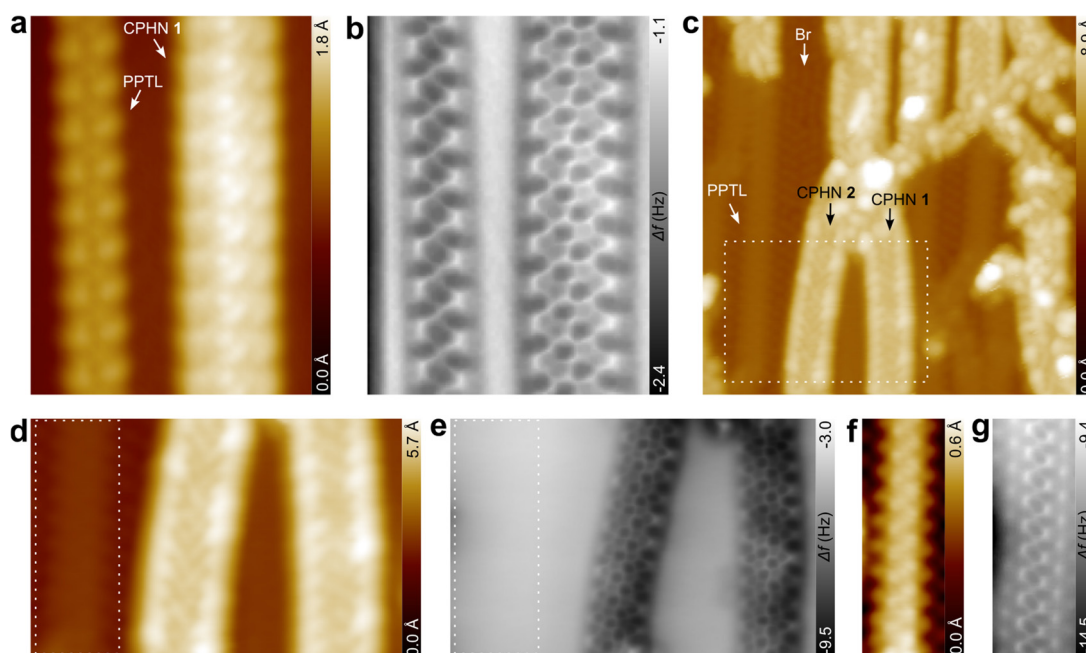
Fig. R1 | Vibrational modes of CPHNs. **a,b**, Tip-enhanced Raman spectra of CPHN **1** (**a**) and CPHN **2** (**b**) acquired in contact mode at the positions indicated by the correspondingly colored dots in the insets. For comparison, the simulated TERS spectra of CPHN **1** and CPHN **2** (shown in black) are also presented. **c,d**, The schematics of representative vibrational modes for CPHNs **1** (**c**) and **2** (**d**), respectively. The color intensity gradient of each atom reflects its contributions to the modulus of the vibrational eigenvectors, i.e., the darker the color, the greater the atomic contribution to the vibrational mode.

3. While discussing the intrinsic properties of CPHNs on the Br adhere layer (Fig. 4c-d, and ED-Fig. 7), it would be more helpful to include the SRPES regarding the Br adhere layer to better support its presence.

Reply: We thank the Reviewer's suggestion that SRPES experiments using Br 3*d* core levels could better support the presence of a Br adlayer. However, such measures would only confirm the chemisorption of Br adatoms on the Ag(111) surface and do not sufficiently demonstrate the presence

of Br atoms beneath the CPHNs. Therefore, instead of SRPES, we conducted comparative nc-AFM imaging to clarify the adsorption heights of CPHNs and PPTLs before and after Br intercalation. We have added these results in **Supplementary Fig. 16** and incorporated the discussion in the **Supplementary Section 9**.

As shown in **Supplementary Fig. 16a,b**, the STM and nc-AFM images within the same frame for PPTL and CPHN **1** adsorbed on Ag(111) reveal nearly identical adsorption heights. However, after Br intercalation, the apparent height of CPHNs is significantly higher than that of PPTLs in the STM image (**Supplementary Fig. 16c**). **Supplementary Fig. 16d** shows the zoomed-in constant-current STM image of the marked frame in **Supplementary Fig. 16c**. We use the tip height at the STM setpoint conditions of -5 mV and 20 pA as a reference. In the constant-height nc-AFM image within the same frame (**Supplementary Fig. 16e**), only CPHN **1** and **2** remain resolvable, but the PPTL become almost invisible, where the tip height was set at +10 pm. **Supplementary Fig. 16f,g** further show the zoomed-in constant-current STM image and constant-height nc-AFM image, respectively, for the PPTL in the marked frame in **Supplementary Fig. 16d**. It is noticed that, in the constant-height nc-AFM measurement, the tip height was set at -240 pm (the tip was approached by 240 pm to the surface with respect to the tip height at the STM setpoint conditions of -5 mV and 20 pA). Compared to the PPTL observed simultaneously with the CPHNs at the same height (**Supplementary Fig. 16b**), the difference in heights between the PPTL and CPHNs directly indicates that the CPHNs are lifted by an adhered layer of Br, while the PPTL is not. Moreover, based on the height change of the AFM tip, the estimated thickness of the adhered Br layer is approximately 250 pm, which is consistent with the atomic size of Br and supports the model of a single-layer Br intercalation beneath the CPHNs.



Supplementary Fig. 16 | Comparison of the adsorption heights of CPHNs and PPTL before and after the Br intercalation.

4. The manuscript shows the domains of PPTL chains (ED-Fig. 4), however, further clarification of the ratio of the two isomeric CPHNs (Fig. 3a), as well as the yield and limiting factors for the fusion reaction would strengthen the synthesis section. Additionally, a theoretical perspective on factors that limit the width growth in CPHNs (ED-Fig.2c) would be valuable.

Reply: We appreciate the Reviewer's constructive suggestions. Based on the statistical analysis of STM images in **Supplementary Fig. 5**, including a total of 49 CPHNs, we have determined a 26:23 ratio for CPHN 1 and 2. Moreover, we optimized the coverage, annealing temperature and duration for the synthesis of CPHNs, the total yield for CPHNs reached 21.8% (11.6% and 10.2% for CPHN 1 and 2, respectively) as derived from the STM images in **Supplementary Fig. 4a-d**.

To investigate the width growth of CPHNs, we conducted additional DFT calculations to evaluate the energy barriers associated with adding a PPTL chain to CPHNs. As shown by the calculated reaction pathways for the fusion of PPTL with both CPHN 1 and [3]CPHN in **Supplementary Fig. 7**, slightly higher reaction barriers of 1.50 and 1.49 eV compared to the value of around 1.23 eV for the fusion between two PPTL chains is revealed. This indicates that C–C bond formation between PPTL chains or between PPTL and CPHNs is not the rate-limiting step in the lateral fusion reaction.

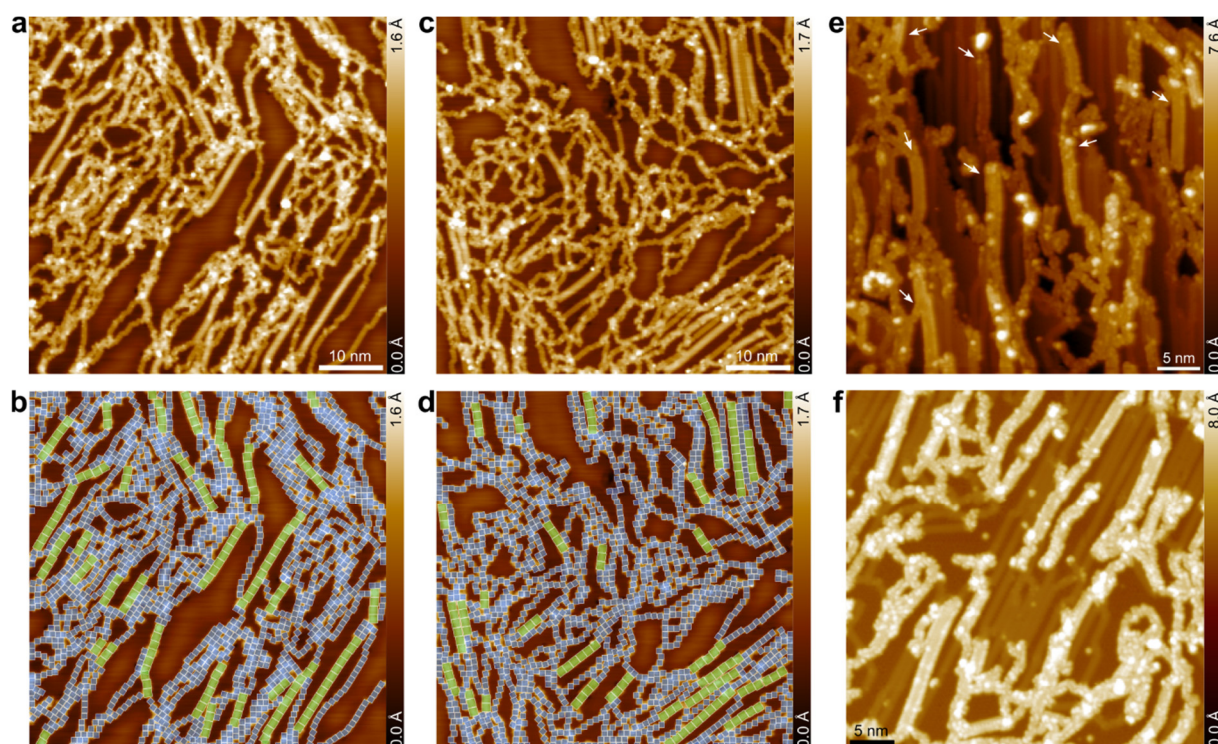
In the initial lateral fusion step, two PPTL chains can be relatively easy to approach each other. However, once a CPHN is formed through the fusion of two PPTL chains, the enhanced rigidity of the newly formed CPHN may restrict it diffusing towards nearby PPTL or other formed CPHNs. It is noticed that as illustrated in **Supplementary Fig. 7c-f**, we consider a model by putting the PPTL with a similar separation between PPTLs as those in Extended Data Fig. 2. However, it is observed that in most cases, the formation of CPHNs may lead to the larger separation of CPHNs from other PPTL or CPHNs, in which such a larger separation may become an additional factor to lower the possibility for their fusion. This can explain the much lower yield of wider CPHNs. Hence, the lower yield of wider CPHNs could mainly be ascribed to the increased separation of the formed CPHNs from a neighbor PPTL chain (**Supplementary Fig. 7a,b**).

We have added these information in the revised manuscript. It reads,

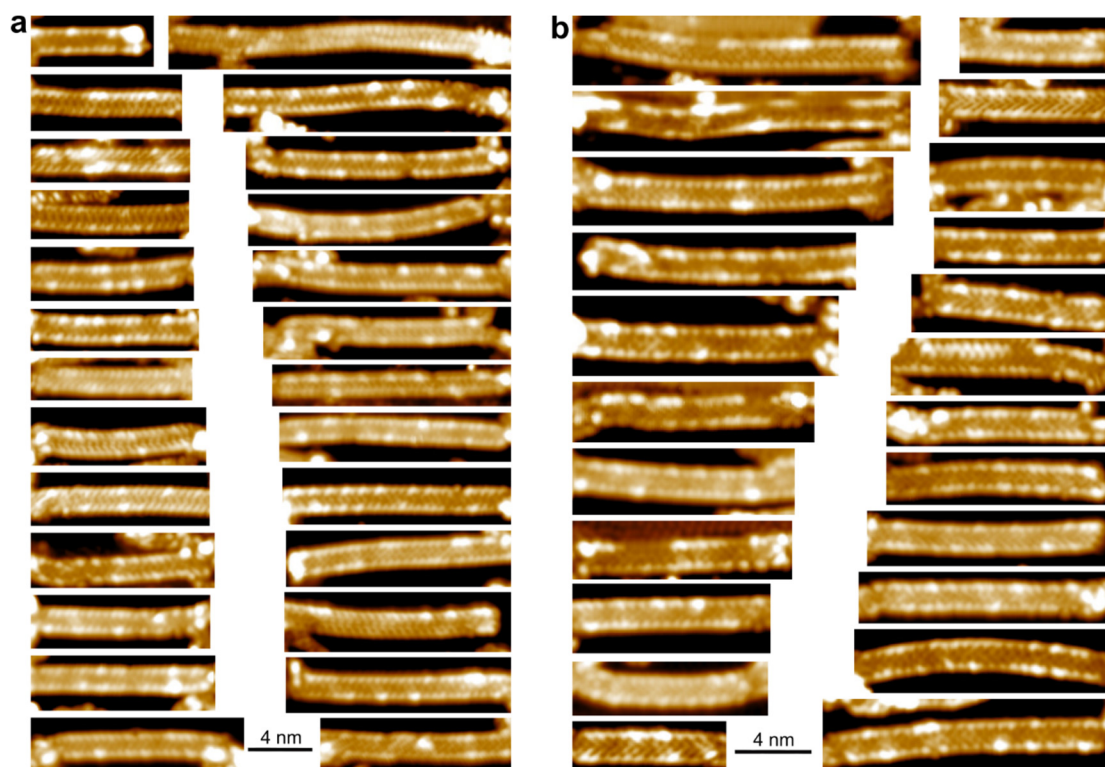
“After annealing the samples with the prepared PPTLs at an elevated temperature of approximately 773 K, wider nanoribbons are formed, typically exhibiting a double width of the PPTL (Fig. 2a, Extended Data Fig. 2a), showing a yield of 21.8% (Supplementary Fig. 4a-d) ...”

“The yield ratio of CPHN 1 to CPHN 2 is approximately 1:0.9 (11.6% and 10.2% for CPHN 1 and 2, respectively) according to the AFM (Extended Data Fig. 2e-k) and STM images (Supplementary Fig. 5), ...”

“Wider CPHNs with a triple-PTTL width ([3]CPHNs) are also observed (Extended Data Fig. 2b–d), but their yield (< 2%) is significantly lower than that of CPHN 1 and CPHN 2. The lower yield of wider CPHNs could mainly be ascribed to the increased separation of the formed CPHNs from a neighbor PPTL chain (Supplementary Fig. 7a). The CI-NEB calculations show that the enhanced rigidity of CPHNs is an additional factor for the slightly increased lateral-fusion reaction barriers between a PPTL and a CPHN (Supplementary Fig. 7c-f). Ag(111) is found to be the most appropriate surface for the production of CPHNs among various coinage metal surfaces (Supplementary Section 5 and Supplementary Fig. 8).”



Supplementary Fig. 4 | Statistical analysis of CPHN yields.



Supplementary Fig. 5 | Statistical analysis of the yield ratio between CPHN 1 and 2.

5. For the structures of PPTL (Fig.2) and the wide CPHN (ED-Fig.2c), could the authors investigate their electronic structures and compare the distinctions in electronic behavior associated with varying widths?

Reply: For PPTL, we have included the theoretical calculations (**Fig. 3a**) and transport measurements (**Supplementary Fig. 10**). While the calculations suggest that PPTL is a narrow bandgap semiconductor, in agreement with the transport measurements in **Supplementary Fig. 10e**. Due to the difficulty in decoupling PPTL from the substrate, not as CPHNs (**Supplementary Figs. 15,16**), it is still difficult to measure the intrinsic electronic properties of PPTL using STS measurements. Despite this experimental challenge for PPTL, fortunately, the good agreement of experimentally measured electronic properties of CPHNs (**Fig. 4**) with the theoretical results (**Fig. 3**) may provide indirectly a support for the calculated electronic properties of PPTL, since PPTL is the basal components of CPHNs. In particular, the TB calculations and analysis clearly reveal the electronic properties of CPHNs originating from those of PPTLs.

We have conducted theoretical and experimental studies on electronic property of wider CPHNs. Specifically, two CPHNs with triple PPTL width (denoted as [3]CPHN) on Br/Ag(111) were experimentally measured (**Extended Data Fig. 10g-m and Supplementary Figs. 21,22**) and theoretically calculated using spin-unpolarized DFT with different aligned PPTLs (**Extended Data Fig. 10a-f**). In the dI/dV maps of the measured [3]CPHNs (**Extended Data Fig. 10m, Supplementary Fig.22f-j**), the striped patterns are similar to those in CPHN 1 and 2 (**Extended Data 8e,l**). Our calculations show that in all configurations of [3]CPHN the band structures give similar metallic bands as those in CPHN 1. This allows to predict that [3]CPHN is metallic, which can be attributed to the breaking of nonsymmorphic symmetry in all types of [3]CPHN (**Extended Data Fig. 10a-c**).

In the revision, we have rewritten the related paragraphs. For PPTL, we have added sentences. It reads, “The I - V curves and their numerically derived dI/dV spectra indicate that PPTL is a narrow bandgap semiconductor, exhibiting a zero-conductance gap of about 50 meV (Supplementary Fig. 10), much smaller than that of CPHN 2.”

For [3]CPHN, we have added comparison with other CPHNs. It reads, “In sharp contrast to the commonly semiconducting properties typically observed in narrow GNRs due to quantum confinement

effects, CPHN 1 maintains its unique metallic property despite its narrow width, owing to its distinctive structure. Furthermore, all types of [3]CPHNs formed with three PPTL widths are predicted to exhibit metallic behaviour regardless of the PPTL fusion orientations, based on the presence of bands B_1 and B_2 similar to those observed in CPHN 1 (Extended Data Fig. 10, Supplementary Section 13). This metallic character arises because the nonsymmorphic symmetry is broken in both CPHN 1 and [3]CPHNs, unlike in CPHN 2. ”

6. In the tip-lifting measurements (Fig.4e-i, and ED-Fig.10), have the authors conducted tests with different ribbons? This would mitigate potential influences from extraneous factors, such as materials adhered to the tip (ED-Fig.10a, the top bright region next to CPHN 1), or variations at the opposite ends of the ribbon (ED-Fig.10b)?

Reply: Yes, we have conducted transport experiments on different CPHN 1 and CPHN 2 samples. As discussed below, variations in the tip-ribbon contact or the terminal structures of the CPHNs would alter the contact resistance and therefore influence the absolute transport conductance. Even though, the order of magnitude and the decay constant β remain largely unchanged throughout the lifting experiments of different samples of CPHN 1. Some additional results have been added in **Supplementary Fig. 9** incorporative with the results in **Extended Data Fig. 4**. For comparison, the measurements and data for PPLT have also included in **Supplementary Fig. 10**.

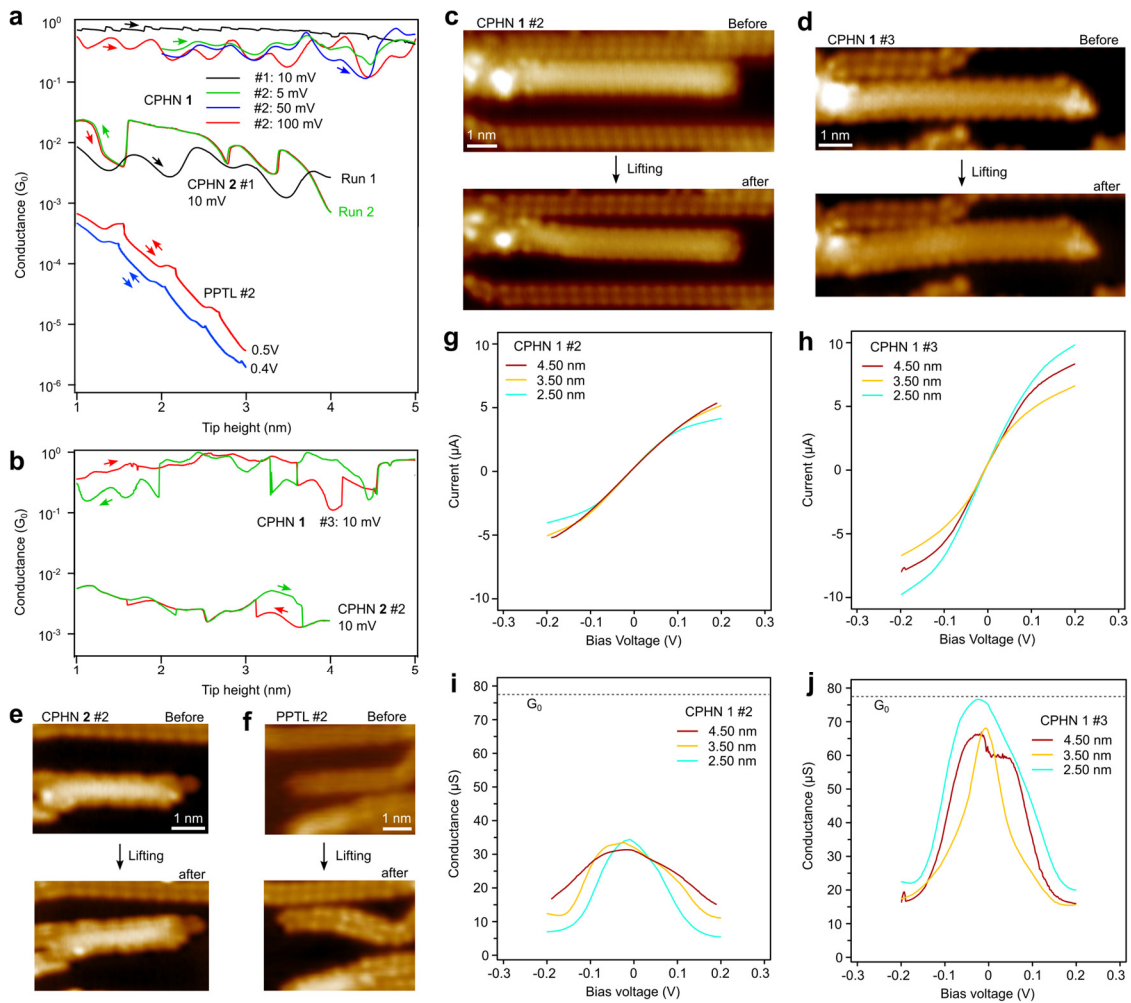
As shown in **Supplementary Fig. 9a**, the stable lifting experiment of CPHN 1 #2 (STM image in **Supplementary Fig. 9c**) exhibits an average conductance of around $0.5G_0$, which is slightly lower than the CPHN 1 #1 ($0.9G_0$) in the main text (**Fig. 2i**) but still within the same orders of magnitude for each type. Moreover, the decay constant (β) remains largely identical, showing almost no decay (red curve) up to 4 nm for the lifted CPHN 1.

The change in contact resistance due to variations in the tip-ribbon contact has been directly observed in the lifting experiments of CPHN 1 #3 and CPHN 2 #2, as shown in **Supplementary Fig. 9b**. The conductance of CPHN 1 #3 recorded during a reversal up and down tip trace exhibits conductance jumps from an average level of $\sim 0.3G_0$ to $\sim 0.8G_0$. This observation strongly suggests that the sticking strength between the tip and the CPHNs is very important, where the slight change between them may highly affect the measured conductance. Moreover, for CPHN 2 #1, two independent lifting

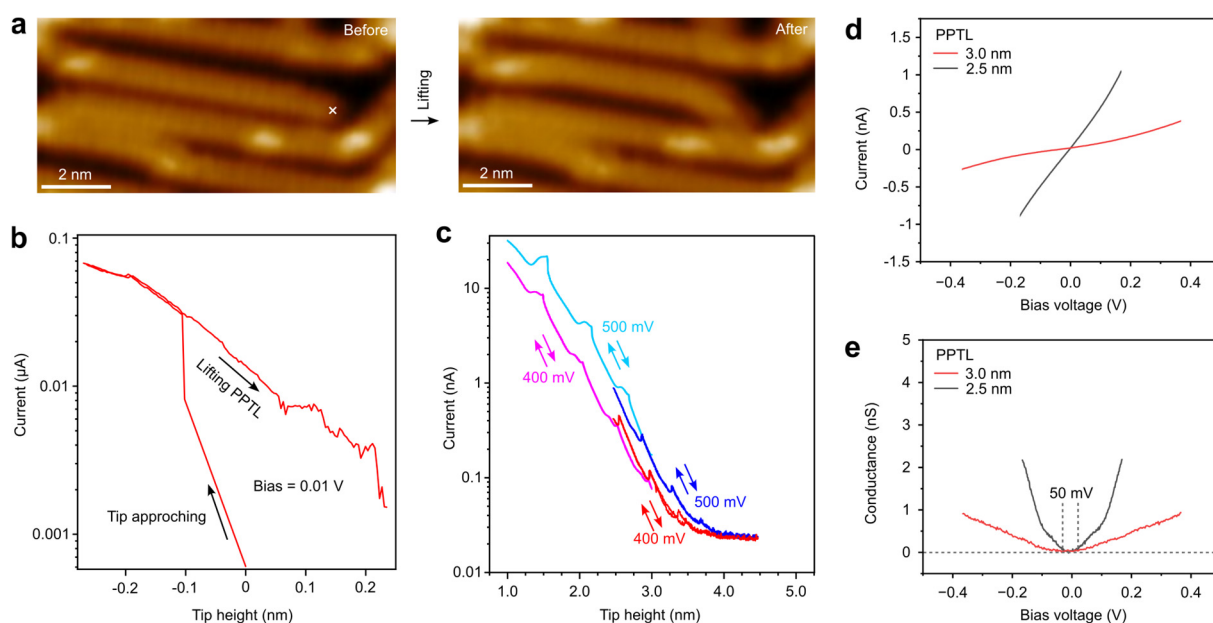
experiments on the same CPHN 2 (run 1 and run 2) are shown, each exhibiting a distinct tip–ribbon contact, the conductance of which however are still in the same order of magnitude and show similar decay constant (β).

Note that in the transport measurements, we first had the tip contacted with a CPHN or PPTL at an end by tracing the tunneling current (**Extended Data Fig. 4c,d**). After their contact, we had the tip continued downwards with a recorded height change of about 0.1~0.2 nm. This procedure can have the tip more strongly sticking to the CPHNs or PPTL and commonly result in relatively stable conductance during the manipulation.

We have added these additional results in **Supplementary Figs. 9,10** and the related discussions in **Supplementary Section 6**.



Supplementary Fig. 9 | Transport Measurements of Additional CPHNs.



Supplementary Fig. 10 | Lifting experiments of PPTL.

7. Finally, the authors need to explain why the contact resistance in the lift-off experiments is surprisingly small. STM break junction experiments routinely suggest that the tip-molecule interface is the limiting constraint on the effective through conductance. The fact that the authors observe values close to G_0 is inconsistent with a large body of work suggestion that the contact resistance for the suggested geometry should limit the conductance to $\sim 10^{-2} G_0$.

Reply: The Reviewer is correct that in break junction the tip-molecule interface is the limiting constraint on the effective through conductance, which could be from the atomic contact at the tip-molecule interface, commonly formed through adsorption of molecule in the junction.

However, in our experiment, we used a specific procedure in preparation of the so-called two-electrode device. As shown in **Extended Data Fig. 4**, we had the tip approaching to the sample at one end of CPHNs or PPTLs, by pre-setting a distance of 0.2~0.3 nm, with respect to the initial height (at STM setpoint of -0.1 V and 10 nA). **Extended Data Fig. 4c,d** shows the recorded tunneling current. The rapid increase of current indicates the tip-molecule contact, followed by a relatively slow increase of current to a certain value with tip further approaching. This procedure could lead to a high possibility to pick up the ribbon or PPTL at the end and have the tip-molecule strongly stuck during lifting the tip. During lifting, the maintained observation of current thus indicates that the ribbon or PPTL has been picked up at the end. The pre-set approaching distance of about 0.2~0.3 nm was found to be appropriate for the ribbon manipulation in our experiment. Too small tip approaching distance may lead to the too

weak sticking and lead to the drop of molecules, but too large approaching distance may damage the sample or the tip. For CPHNs, such procedure is necessary to perform the transport measurements. For PPTLs, it turned out to be much easier to be picked up than CPHNs, which could be ascribed to their soft nature of polymers compared to the relatively rigid CPHNs. To have the results comparable, we performed similar approaching distance both for CPHNs and PPTLs. It is noted that the tracing currents of CPHN **2** and PPTL have already rapidly decreased during their lifting, which can be ascribed to the relatively large decay constant β , compared to negligible decay in CPHN **1**, as observe in **Fig. 2i**.

We believe this specific procedure has already had the tip-ribbon strongly stucked, in sharp contrast to the atomic contact in commonly break junction experiments. Therefore, the observed conductance close to G_0 in our experiment may benefit from this strong sticking at the tip-ribbon interface by overcoming the atomic contact limitation.

In the revised manuscript, we have included such information in **Supplementary Section 6**.

Additional minor points for consideration in the main text or SI include:

1. Could the authors clarify the yields for the wet-lab synthesis and provide the carbon NMR spectrums in Supplementary Information Part 1?

Reply: We appreciate the reviewer for highlighting this point. We have now included the yields of the solution-synthesized **1,2,5,6-tetrabromocyclooctane** and **1,5-dibromo-1,5-cyclooctadiene (DBCOD)** in the reaction scheme, as well as in the text of the *Supplementary Methods*.

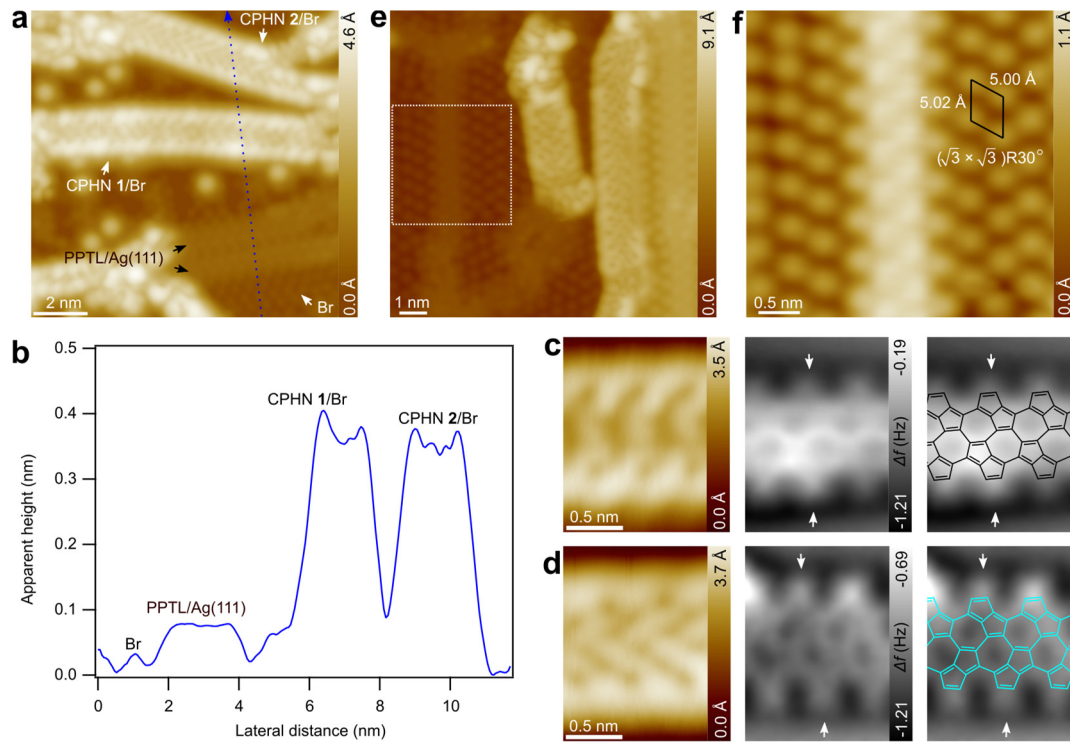
Regarding the carbon NMR spectra, since the synthetic procedure and the resulting products (*1,2,5,6-tetrabromocyclooctane* and *DBCOD*) are well-documented in the literature [**Eur. J. Org. Chem. 2014, 7566-7571**], we have only provided the hydrogen NMR spectrum for confirmation. If the reviewer is interested in the carbon NMR spectrum of *DBCOD*, the aforementioned literature contains detailed information.

Additionally, we have cited this original reference in the *Supplementary Methods* section and included the following statement: "The synthesis of 1,5-dibromo-1,5-cyclooctadiene (DBCOD) was performed via solution-phase chemistry following the procedure reported in previous work [**Eur. J. Org. Chem. 2014, 7566-7571**], as detailed below."

2. In ED-Fig.7, are the structures shown PHCN or CPHN?

Reply: We appreciate the reviewer's thorough review of our manuscript.

We have corrected the typos. Due to much more important information has to be included in Extended Data, the former ED-Fig.7 has been revised, and moved into SI, as **Supplementary Fig. 15**, Some related data are also given in **Supplementary Fig. 16**.



Supplementary Fig. 15 | Insertion of Br adlayer between CPHNs and Ag(111).

3. In ED-Fig.8 and 9, it would be useful to include Br/Ag(111) substrate spectra as a reference to identify features in the dI/dV spectra.

Reply: We appreciate the reviewer's suggestion. We have replaced the single dI/dV spectra in the original Fig. 4 and Extended Data Figs. 8 and 9 with 2D LDOS maps and their Fourier-transformed data, which better support the band structures of CPHNs.

It is recommended that the authors address these issues to strengthen the manuscript further. It will be a great contribution to this field.

Reply: We are grateful to the Reviewer for the insightful suggestions and for appreciation of our work.

Referee #2 (Remarks to the Author):

Report on manuscript "Realising narrow carbon pentaheptite nanoribbons with strong metallicity" by Jianmin Huang et al.

This manuscript reports the on-surface synthesis and characterization of so-called pentaheptite nanoribbons, which are highly unusual in the sense that they consist of 5- and 7-membered rings only, in contrast to the well-established 6-membered ring graphene nanoribbons. Interest in such structure derives from early predictions of metallicity in extended, 2D pentaheptite and the prospect of achieving carbon-based nanoscale metallic electrodes and interconnects for replacing (or complementing) traditional metals in devices.

Using a cyclooctadiene precursor, the authors report on an interesting reaction pathway that transforms linear polycyclooctadiene chain into a linear pentalene polymer on a Ag(111) surface under ultrahigh vacuum conditions upon annealing to 400 °C. Further annealing to 500 °C is found to induce the lateral fusion of neighboring polypentalene oligomers, resulting in two different variants of narrow pentaheptite ribbons, which distinguish themselves by the relative orientation of the pentalene units.

The manuscript presents a thorough structural characterization of the pentaheptite ribbons produced in this way. Results from scanning probe methods (STM, nc-AFM with CO-functionalized tip) complemented by DFT-based simulations clearly reveal the 5- and 7-membered ring topology of the ribbons. Vibrational spectroscopy, performed by in-situ tip-enhanced Raman spectroscopy, is somewhat less convincing, because calculated and measured spectra are in relatively poor agreement. The most significant shortcoming of the manuscript, however, is the part aimed at demonstrating "strong metallicity" of one of the two pentaheptite ribbon variants. The authors present both differential conductance scanning tunneling spectroscopy data and two-terminal transport data (from STM tip lift-off experiments), but their discussion of metallicity ultimately relies heavily on a quantitative comparison to DFT calculations, which is problematic, as outlined below.

Reply: We are grateful to the Reviewer for the thorough review and insightful feedback on our work. The reviewer's constructive comments have been addressed in detail, as outlined below. Specifically, we have carried out quasiparticle interference (QPI) measurements to map the band structure of the CPHNs. This additional data provides further experimental evidence supporting metallic behavior of CPHN 1.

For the calculated Raman spectroscopy, the agreement between the calculated and measured spectra are improved by including the substrate and the plasmon field effect instead of the previous results just considering free-standing CPHNs. However, as suggested by the reviewer, we removed the TERS part from this manuscript into separated studies. The details are given below in point-by-point response.

First of all, DFT (also at the PBE level of theory) is well known to underestimate band gaps. A one-to-one comparison of dI/dV spectra with calculated DOS, on the same energy scale (such as in Fig. 4, or ED Fig. 8 and 9), is not per se meaningful. In particular, the presence of a peak roughly in the energy region where DFT also predicts a peak in the DOS, cannot be taken as evidence that the computed band structure actually describes the situation of the experiment. In Fig. 4, for instance, the computed DOS actually agrees poorly with the experimental dI/dV spectra, which exhibit many more peaks than the DOS.

Reply: We are grateful to the Reviewer's insightful comments. We agree that a direct comparison between the dI/dV spectra and the calculated density of states (DOS) is not fully convincing in demonstrating the metallicity of CPHN 1. Specifically, the DFT calculations were based on infinitely long, periodic CPHN structures, which may not accurately capture the finite lengths and distinct terminations present in the experimental samples. To address this, we have conducted DFT calculations on CPHN structures with finite lengths and varied terminations. The results from these more realistic models show good agreement with the newly obtained quasiparticle interference measurements, as detailed in our response below.

A proper way of identifying from which bands derive peaks observed in the dI/dV spectra would be via LDOS maps (DFT) and dI/dV maps (experiment). The authors provide this to some extent in Ext. Data Fig. 8 and 9, but the agreement is quite poor. A notable example is the comparison in Fig. 9g vs Fig. 9h, where both maps do show bright maxima but at significantly different spatial locations. Also, the energies chosen for comparison appear somewhat arbitrary, and their choice is not explained.

Given the questionable comparison of experimental data with DFT calculations, the data shown in the manuscript are not sufficient to support the main claim of the manuscript, which is metallicity of the pentaheptite nanoribbons. The authors would rather need to refer to mapping the energy-dependent standing waves formed in finite-length ribbons, which can be Fourier-transformed into reciprocal space

to provide the dispersion relation of the underlying band structure. If the ribbons are metallic, one (or several) of the resulting bands will be seen to cross the Fermi energy.

Reply: We sincerely thank the Reviewer for pointing out these issues. We have revised our manuscript by providing more experimental data and theoretical calculations and analysis. These weaknesses have been addressed in the revised manuscript. The new results can be found in **Fig. 4**, and **Extended Data Figs. 8,9**, and **Supplementary Figs. 19,20**.

We acknowledge that the LDOS maps from our DFT calculations and the experimental dI/dV maps presented in the previous manuscript were not fully consistent in terms of the spatial features. This discrepancy can be attributed to the differences between the model structures used in the DFT simulations (infinite lengths) and the actual experimental conditions (finite lengths). For CPHNs with finite lengths in the experiments, the dispersive band crossing the Fermi level is expected to exhibit energy-dependent standing waves, leading to periodic patterns of minima and maxima in the dI/dV maps. However, these spatial variations were absent in our previous DFT calculations based on infinitely long CPHN structures. To address this, we have performed LDOS simulations using CPHN models with the finite lengths corresponding to the experimentally measured ones. The results from these revised simulations show improved agreement with the experimental dI/dV maps.

Following the Reviewer's suggestion, we have successfully performed quasiparticle interference (QPI) measurements for both CPHN **1** and **2** on the Br/Ag(111) surface. As shown in the revised **Fig. 4** in the main text and the response to comment #7 below, we clearly observe a dispersive band crossing the Fermi energy for CPHN **1**. We believe that these QPI results provide compelling evidence for supporting the metallicity of CPHN **1**. Please see the details in point-by-point response below.

A major drawback of the pentaheptite nanoribbon fabrication via lateral fusion of oligomers is that it is not a deterministic process that results in atomically precise nanoribbons, but rather in a mixture of differently fused (and non-fused) structures, having different widths, lengths and electronic properties. While this does not compromise the fundamental interest in metallic all-carbon nanoribbons, it clearly prohibits any claims about applicability in devices. The limited quality of the pentaheptite ribbons raises the question whether the yield of the targeted structure(s) can be increased by optimization of the synthesis parameters? Maybe by using a template surface such as Au(110), which may align the chains

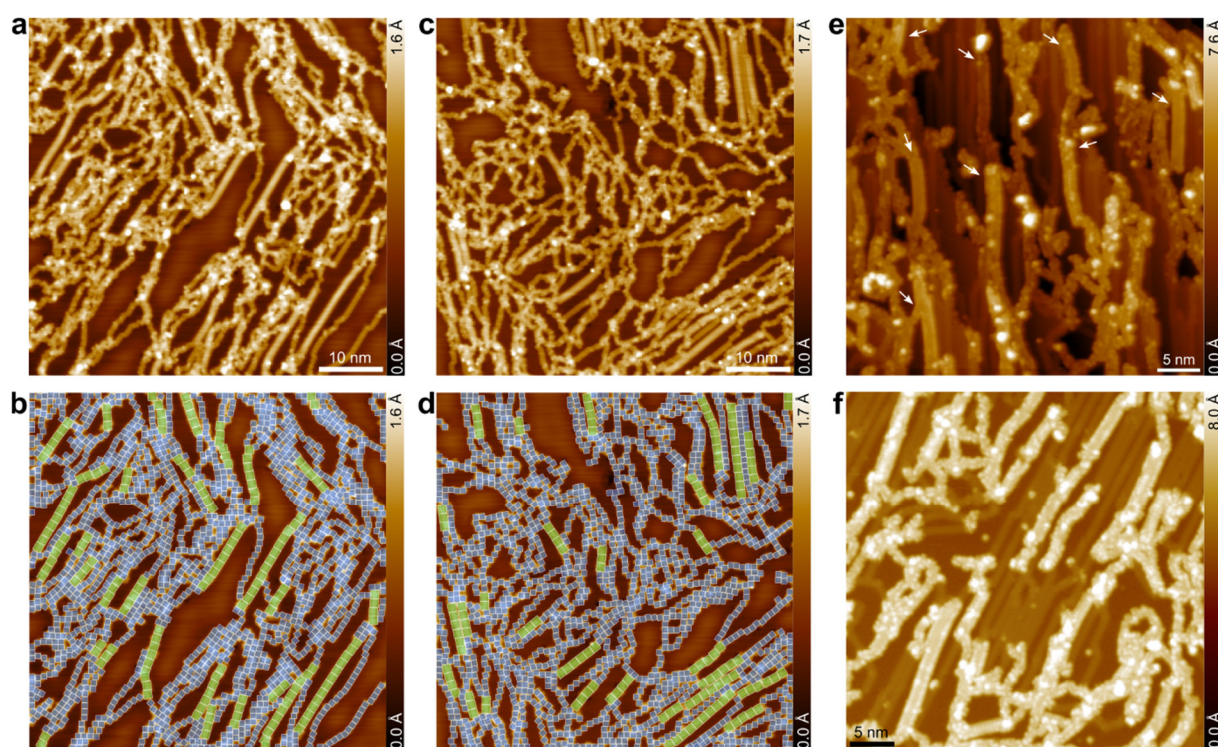
and potentially enhance the quality of the fused chains?

Reply: In the previous version of our manuscript, we focused more on the realization of CPHNs rather than their yield. However, after optimizing the fabrication conditions (a full monolayer DBCOD and an annealing temperature of 773 K for duration of 2 hours after PPTL formation), we have been able to significantly enhance the yield of CPHNs. As shown in **Supplementary Fig. 4a-d**, the total yield of CPHNs is about 21.8% (11.6% and 10.2% for CPHNs **1** and **2**, respectively). While this yield is somewhat lower compared to the on-surface synthesis of some of the most successful graphene nanoribbons (GNRs), such as 7-AGNR and 9-AGNR, as pointed out by the reviewer, it does not compromise the fundamental interest in metallic all-carbon nanoribbons. The developed synthetic protocol for CPHNs is still in its early stages, and this work represents the first successful realization of these unique structures. Even at this early stage, the vision of using CPHNs as a potential replacement for metal electrodes in carbon-based devices remains reasonable. Importantly, we believe that the yield and selectivity of CPHNs could be further enhanced through more optimized conditions and the use of better-designed precursors.

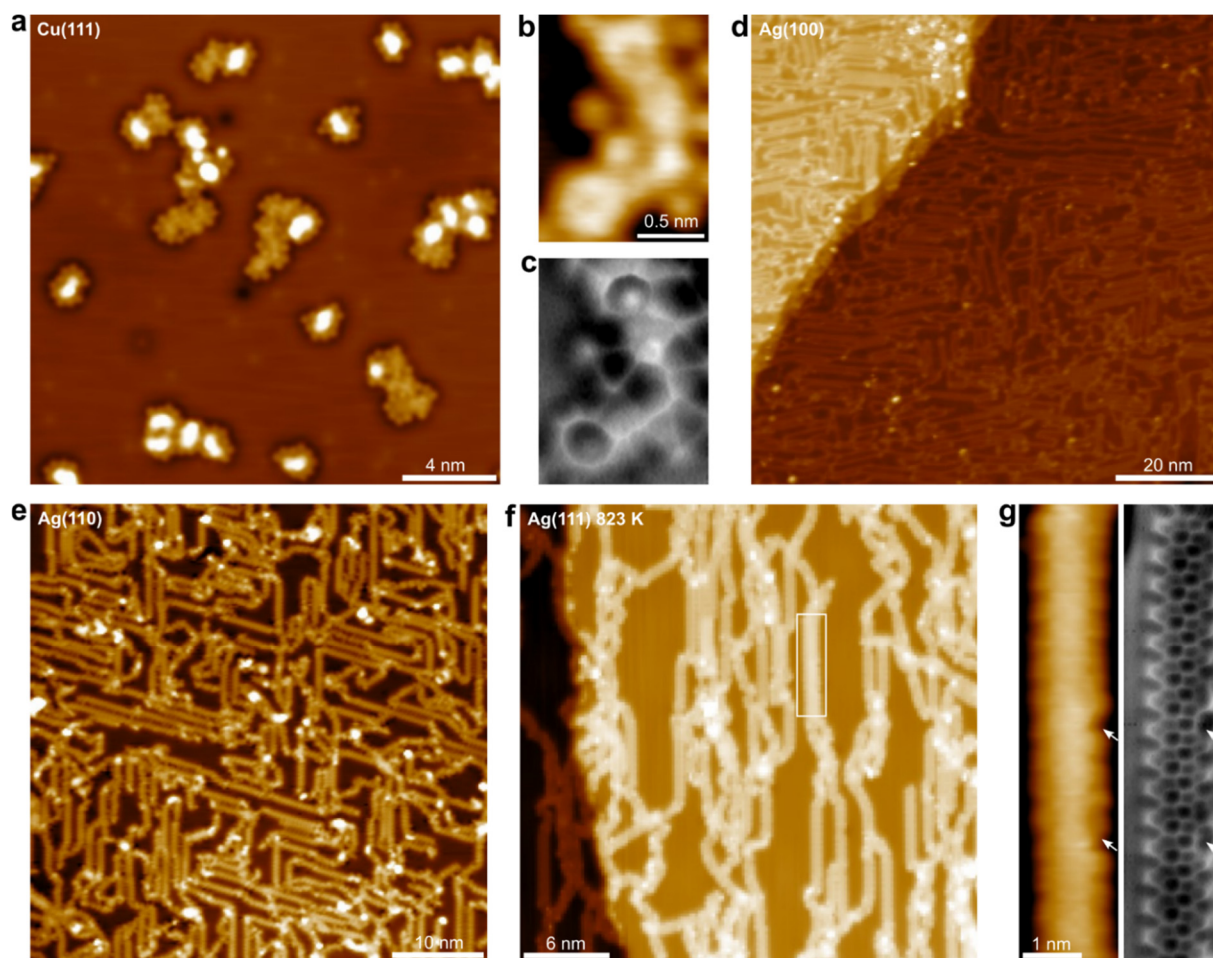
In addition to Ag(111), we investigated several other coinage metal surfaces for the on-surface synthesis of CPHNs from the DBCOD precursor monomer, including Cu(111), Ag(100), Ag(110), Au(111), Au(110), and Au(100). Due to the relatively low molecular weight of the DBCOD monomer, it readily desorbs 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.

Despite the limited yield of CPHNs achieved in the current work, their realization represents a significant step forward. The theoretical prediction of these unique all-carbon nanoribbons has been a

long-standing goal for nearly 30 years since the initial theoretical work in 1996. While the current yield may be somewhat lower compared to other graphene nanoribbon systems, the fundamental interest and potential applications of metallic CPHNs remain compelling. We believe that further optimization of the synthetic conditions and precursor design will enable enhanced yield and selectivity of these promising carbon nanostructures in the near future.



Supplementary Fig. 4 | Statistical analysis of CPHN yields.



Supplementary Fig. 8 | Attempts of optimizing the synthesis of CPHNs using different surfaces and annealing temperatures.

Overall, given the lack of compelling evidence for the claimed metallicity and the polydispersity of the obtained ribbon products, I cannot recommend publication of this manuscript in Nature. Before submitting to a more specialized journal, I suggest the authors to consider the points outlined below.

Reply: We appreciate the reviewer's constructive suggestions, and we have carefully considered these suggestions. To address the concerns regarding the claimed metallicity of CPHN **1**, we have provided compelling evidence from QPI measurements that strongly support this claim. Regarding the polydispersity of the CPHNs, we acknowledge this as a primary concern for their potential applicability in device fabrication. In the revised introduction, we have clarified that the realization of metallic CPHNs represents a promising candidate material for future all-carbon-based electronics, while also noting that additional development, such as transferring the CPHNs onto semiconductor substrates, is still required before direct device fabrication. The focus of this study is on the fundamental

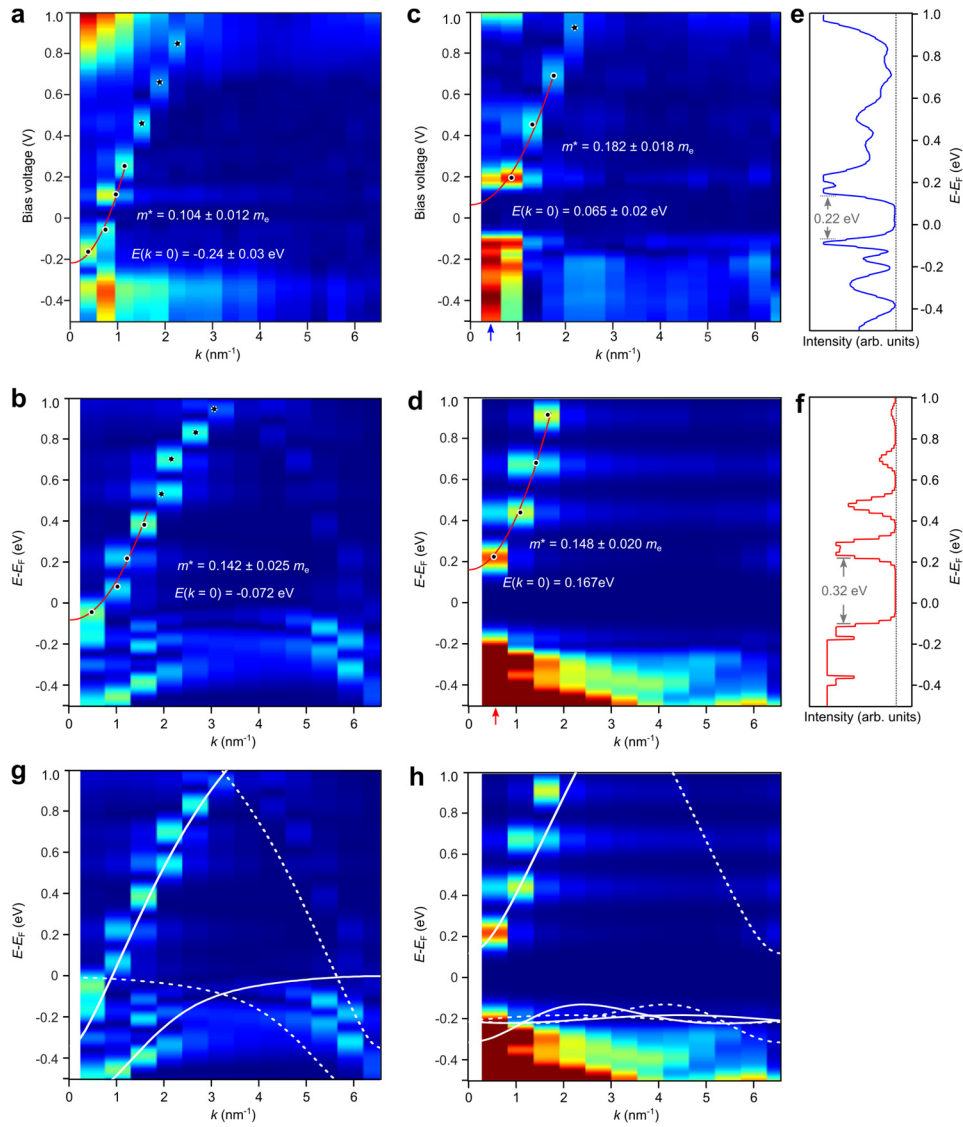
demonstration of a novel metallic CPHN, which lays the groundwork for potential future applications in all-carbon devices. It is our sincere hope that the Reviewer will find that the concerns have been adequately addressed. We appreciate the opportunity to revise and strengthen the manuscript, and we look forward to your further feedback.

1. I am somewhat puzzled by the computed band structures of CPHN 1 and 2 on Br/Ag(111). Considering the significant electronegativity of Br, I am surprised how closely the band structures of CPHNs on Br/Ag(111) resemble those of the gas phase species. This seems to be very different than in the case of Cl/Au(111), which strongly dopes graphene nanoribbons (see ACS Nano 2024, 18, 26, 16622–16631). Is there a good reason for that? BTW, how are the Fermi energies in the calculations defined/set?

Reply: We thank the reviewer for providing the reference regarding the case of Cl/Au(111). Our DFT calculations suggest a relatively weak interaction between CPHNs and the Br/Ag(111) surface. Bader charge analysis reveals that there is a negligible charge transfer, that is, 0.09 holes from the Br/Ag(111) substrate to CPHN 1, and 0.09 electrons from the Br/Ag(111) substrate to CPHN 2 (**Extended Data Fig. 6, Supplementary Section 9**). The good agreement between the bands obtained experimentally and theoretically is consistent with the negligible doping by the Br/Ag(111) substrate (**Supplementary Fig. 19**).

Compared to the stronger interaction observed for 7-AGNR on Cl/Au(111) in previous studies, it can be explained by considering the fact that Br is less electronegative than Cl and the Ag–Br bond is stronger than the Au–Cl bond. As a result, the electronegativity of Br atoms is more effectively neutralized. Therefore, it is reasonable for the Br/Ag(111) surface exhibiting significantly lower electronegativity than the Cl/Au(111) surface.

The Fermi energy in our calculations is defined as follows. For the freestanding case, since CPHN 1 has a half-filled band, its Fermi level is directly determined by the DFT calculations. For the semiconducting CPHN 2, only the highest fully occupied band is known, so the Fermi level can be set either at the top of the filled band or within the gap. In the case of CPHN on Br/Ag(111), we adopt the Fermi level of the Ag(111) substrate after structural optimization of the CPHNs/Br/Ag(111) adsorbate system.



Supplementary Fig. 19 | The fitting of the experimental and DFT-calculated FT-STs data.

2. I am not convinced that the Raman data are fully understood and properly interpreted, and the authors may consider removing this part from the manuscript and devoting a full paper to this aspect. I am concerned by the fact that the most intense peaks in simulations (1315 cm⁻¹ for CPHN 1, 1385 cm⁻¹ for CPHN 2; but also 1072 cm⁻¹ and 895 cm⁻¹, respectively) are absent in experiment. What is the reason for this? Are the calculations missing something important? If not, this discrepancy sheds doubts on the proper structural model for the CPHNs.

Reply: Thank you for your feedback regarding the Raman data analysis and interpretation. We acknowledge your concerns and agree that the current understanding and interpretation of the Raman data are not fully comprehensive. The discrepancies between the simulated Raman and experimental TERS spectra could be primarily ascribed to the adsorption of finite-lengths CPHNs on the Ag(111)

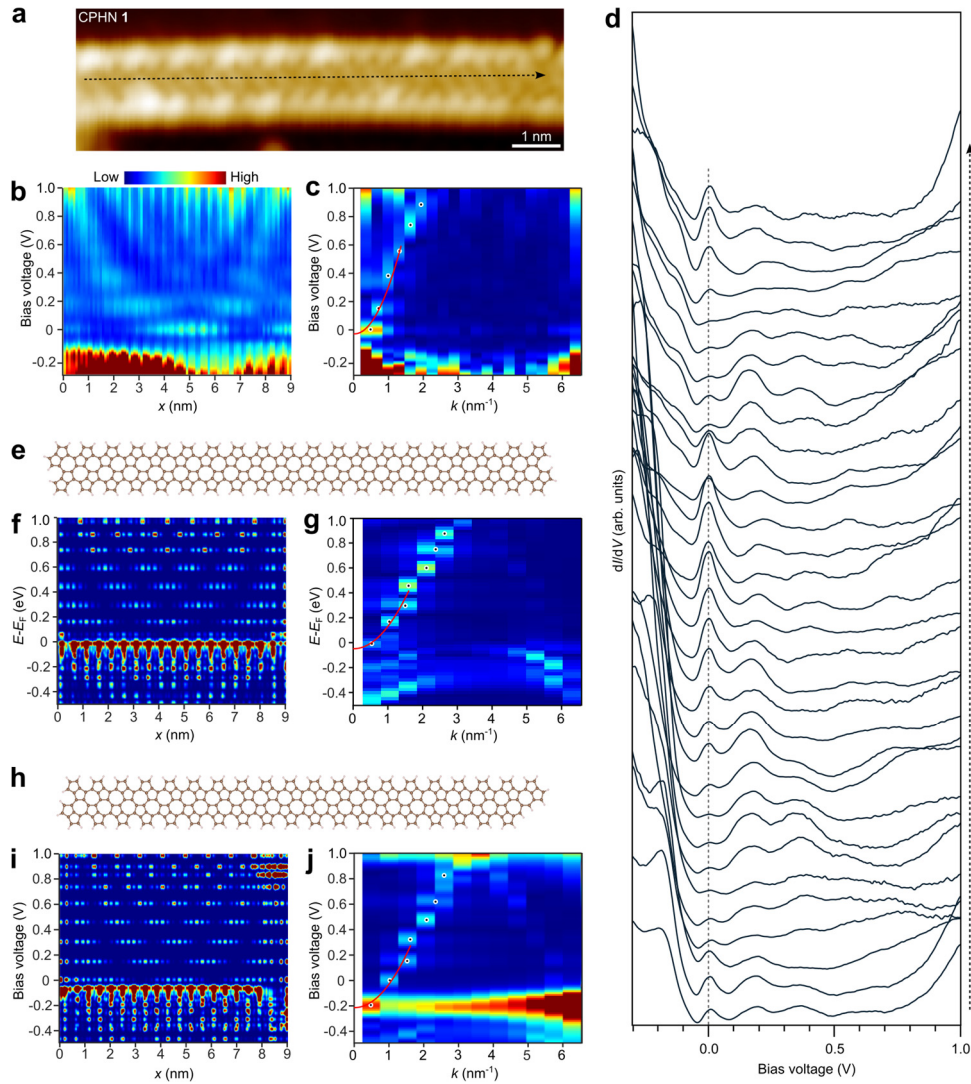
surface and the enhancement of the plasmon Pico cavity, while the current vibration modes are calculated based on free-standing CPHNs with infinite length. To have a better comparison, we have performed additional calculations by including the Ag(111) substrate and the plasmon field of the Pico cavity. The newly calculated TERS spectra are shown in **Fig. R1** (see also reply to comment # from Referee 1), much better agreement has been achieved when compared to the experimental TERS spectra. However, considering the complexity of the influence of the substrate and the picocavity on the vibration modes of CPHNs, we choose to remove the TERS part from the current manuscript, which will be further studied in a separate work.

3. The experimentally observed zero-bias peak in the CPHN 1 chain (Fig. 4 and Extended Fig. 8), attributed to a van Hove singularity (vHS) by the authors, exhibits an unusually narrow linewidth, which is significantly smaller than a typical DOS singularity. This peak rather reflects the characteristics of an inelastic tunneling process, such as Kondo resonance tunneling, rather than an electronic band structure feature. Have the authors considered that this peak could derive from inelastic tunneling? I am curious whether CPHN 1 may contain spin-polarized states along its edges. I would suggest the authors to perform DFT calculations involving spin polarization, and to compare the outcome with the experimental results. Besides, low-bias step features reminiscent of inelastic electron tunneling are also seen around zero bias with an intensity compatible with the zero-bias anomaly (Extended Fig. 8c), again indicating some inelastic tunneling processes via vibrations or spin excitations. Could the authors elaborate on that?

Reply: We appreciate the reviewer for raising these important points. The Reviewer is correct that using single dI/dV spectra is not sufficient. We have conducted additional experiments and theoretical calculations and analysis for better understanding of the nature of the zero-bias peak observed in the chains of CPHN 1, and have compared with the additional results from CPHN 2 and PPTL.

Indeed, there is a van Hove singularity (vHS) due the existence of band extrema near the E_F , as shown in **Figs. 3,4**. However, it is now clear that the previously observed zero-bias peak in the CPHN 1 should not be contributed by the vHS. Instead, the presence of the zero-bias peak in the CPHN 1 can be attributed to the occasional location of the metallic band minimum at the E_F (**Extended Data Fig. 9d**), which is found to depend on the length of CPHN 1, as well as the sites measured along the ribbon. In addition, our spin-polarized DFT calculations show that magnetism in CPHN 1 and 2 on Br/Ag(111)

should be negligible (**Extended Data Fig. 5**). These observations can largely exclude the possible effects from Kondo resonance or other inelastic effects.



Extended Data Fig. 9 | Terminus-dependent band B_1 minimum positions.

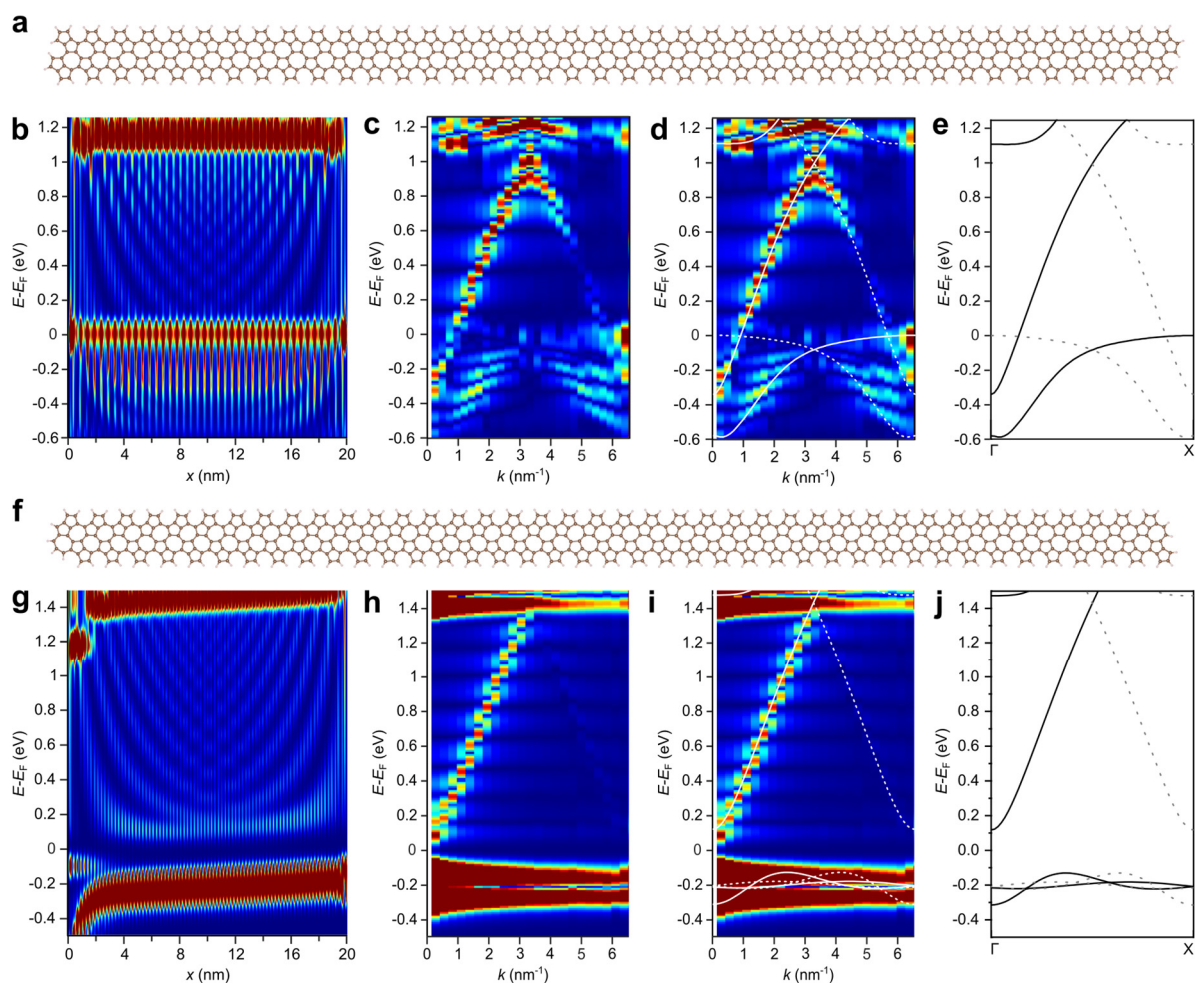
4. Did the author consider finite length effects in the interpretation of their measurements? Judging/guessing from the STM images shown, the STS dI/dV and the contact transport measurements were carried out on short segments with lengths of a few nanometers (less than 10 repeat units?). In this case, one would expect a series of discrete electronic states instead of continuous bands. I therefore recommend performing calculations using finite length ribbon models with effective lengths that match the experiments rather than periodic boundary conditions.

Reply: We sincerely appreciate the reviewer's insightful comments.

In response, we have done the DFT calculations for CPHNs with finite lengths to better align with

the experimental conditions. The results have been presented in **Fig. 4**, **Extended Data Figs. 8,9**, and **Supplementary Fig. 19**, which provide better agreement with the experimental observations from the QPI measurements. Additionally, longer CPHN **1** and CPHN **2** are also calculated (**Supplementary Fig. 20**). These results provide solid support for our claims that CPHN **1** exhibits strong metallicity and CPHN **2** functions as a narrow bandgap semiconductor.

Again, we thank the Reviewer for the insightful suggestions.



Supplementary Fig. 20 | DFT-calculated LDOS and LDOS of CPHN 1 and 2 with 40 units.

5. Also, larger scale STM images showing the ribbons on which dI/dV were taken should be shown in the Supporting Information (e.g. for the ribbons in Fig. 4).

Reply: In the revised manuscript, we have incorporated new results from the QPI measurement of CPHN **1** and **2**, as given in **Fig. 4b,j**.

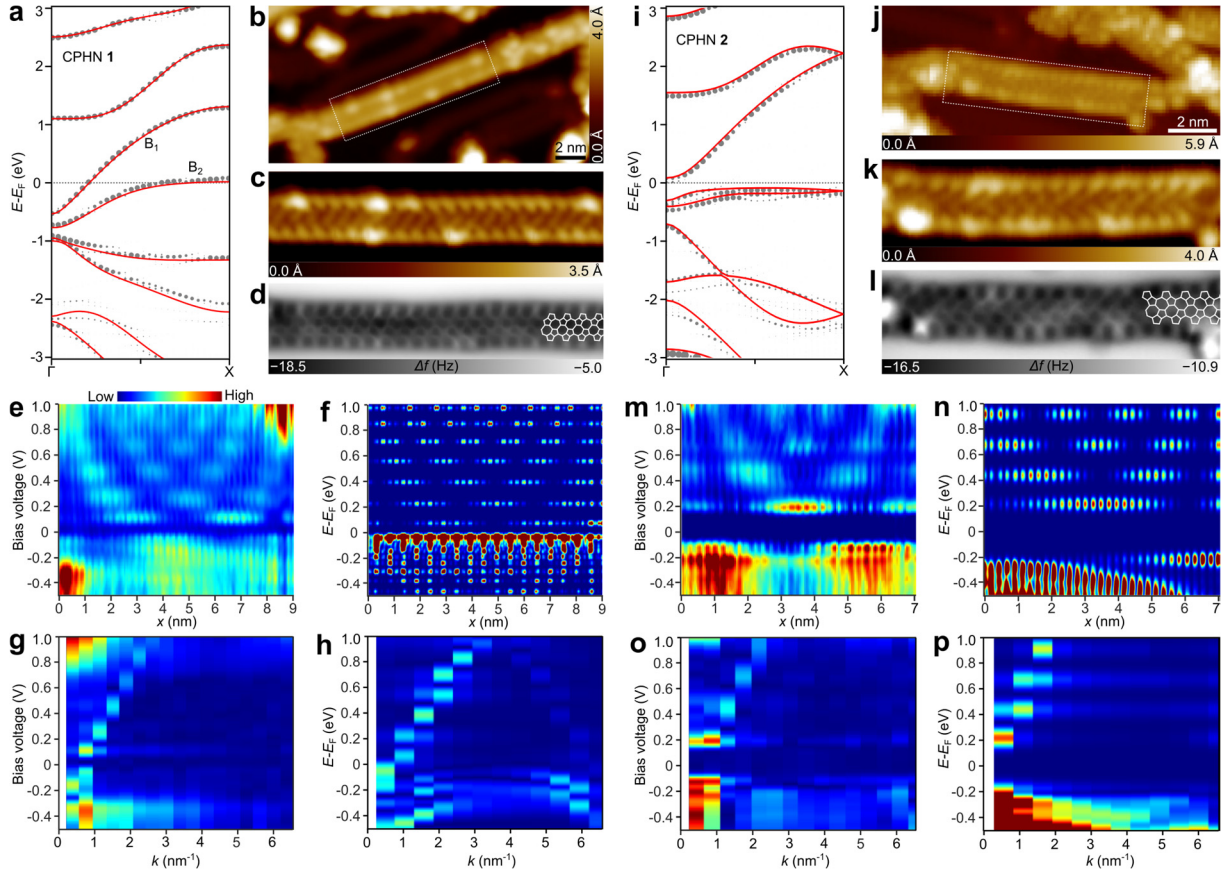


Fig. 4 | Electronic properties of CPHNs 1 and 2.

6. The tip-contact transport results are puzzling. In the case of CPHN 2, the transport measurements show a band shift compared to the STS results, whereas no such shift is observed for CPHN 1. And what accounts for the pronounced broadening of the zero-bias peak, which is an order of magnitude larger than in the STS results? Also, will the end states (are there any?) dominate the transport behavior in such short ribbons? Furthermore, why does the conductance for metallic CPHN 1 and insulating CPHN 2 exhibit almost the same height dependence (slope) in Fig. 4f?

Reply: The numerically-derived differential conductance (dI/dV) obtained from the transport-measured I/V curves with different lifted length may not be used to compare directly with the dI/dV spectra obtained at specific single sites using the tunneling mode. To avoid the confusion, we have just kept the recorded conductance as a function of lifted height in **Fig. 2i**, and have moved the numerical differential conductance with their I/V curves into **Extended Data Fig. 4e-h**.

There are several reasons that such direct comparison is inappropriate. First, the single-site dI/dV spectra reflect the DOSs of the specific sites, while the transport measured I/V curves (with their

numerically-derived differential conductance) are contributed by the integration of the states containing all of the sites in the lifted CPHNs or PPTLs. Second, the states of the sites along the lifted CPHNs or PPTLs may not be uniformly distributed. Say, as illustrated in **Fig. 2h**, bending (or even rotating of bridging bonds, specifically in PPTLs) during lifting may introduce strains, most likely ununiformly distributing along the lifted CPHNs or PPTLs, which can result in certain lifted-length dependent behaviours in I/V curves (and thus in their numerical differential conductance). Such behaviours are more obviously observed in the transport measurements of PPTLs as shown in **Supplementary Fig. 10**, which may also include the rotation of certain bridging bonds due to the polymer nature. Although the bond rotation may not happen in CPHNs, the bending-introduced strains may still lead to the shift of the states along the lifted ribbon, which may be responsible for the broadening of the zero-bias peak in numerically-derived differential conductance of CPHN **1** #1 (**Extended Data Fig. 4g**) and #2,3 (**Supplementary Fig. 9h,j**). In comparison, the peak is much sharp, say, occasionally presented at the E_F in dI/dV spectra taken at specific single sites in tunneling mode (**Extended Data Fig. 9d**). Third, the length-dependent transport may also involve the relatively large decay constant β in the cases of CPHN **2** and PPTL, where the too small current may be out of the measuring range of amperemeter and be recorded as zero, in particular in the lower bias range. This can be ascribed to the observed wider zero-current region in I/V curves (or wider zero-conductance in numerical conductance) with the increasing lifted length of CPHN **2** (**Supplementary Fig. 10e**).

From our fitting, the slope (β decay constant) of the $I(Z)$ curve for CPHN **2** is $0.33 \pm 0.02 \text{ nm}^{-1}$, which remains significantly larger than the β value of CPHN **1** (approaching zero) in the ballistic transport regime (1–3 nm). The conductance decay beyond a tip height of 3 nm for CPHN **1** is attributed to the tip-sample distance exceeding the electron mean free path, leading to the onset of scattering. However, the fitted decay constant $0.25 \pm 0.004 \text{ nm}^{-1}$ is still smaller than the CPHN **2**.

We have included these issues in the revised manuscript.

7. As pointed out above, to demonstrate the metallic character of CPHN **1**, I suggest that the authors apply one-dimensional quasi-particle interference measurements based on line STS measurement. Compelling evidence would be that the Fourier transform reveals the dispersive bands crossing the Fermi level, as predicted in Fig. 4a.

Reply: We sincerely appreciate the reviewer's suggestion. In response, we have successfully conducted quasi-particle interference (QPI) measurements for both metallic CPHN **1** and semiconducting CPHN **2**. The QPI results of CPHN **1** indeed reveals dispersive band crossing the Fermi energy, demonstrated the metallicity of CPHN **1** as expected by the reviewer. We rewrote the electronic structure analysis part of CPHN **1** and **2** and replaced the STS points spectra in the old version with the newly obtained QPI results as shown by the revised Fig. 4.

We have rewritten the section in subtitle of “**Measurements of electronic band structures of CPHNs**” based on these new results, and have also included new data in **Fig. 4, Extended Data Figs. 8,9, and Supplementary Figs. 19,20**.

We are grateful to the Reviewer’s insightful suggestion. In combination with the additional spin-polarized and spin-unpolarized DFT calculations and TB calculations with extended SSH models, as shown in **Fig. 3**, we are confident that we have had compelling evidence to well support our major claims. Moreover, additional measurements and theoretical analysis also allow us to predict that [3]CPHNs (CPHN in triple width of PPTL) are metallic in all types independent on the PPTL fusion orientations (**Extended Data Fig. 10, Supplementary Figs. 21,22**).

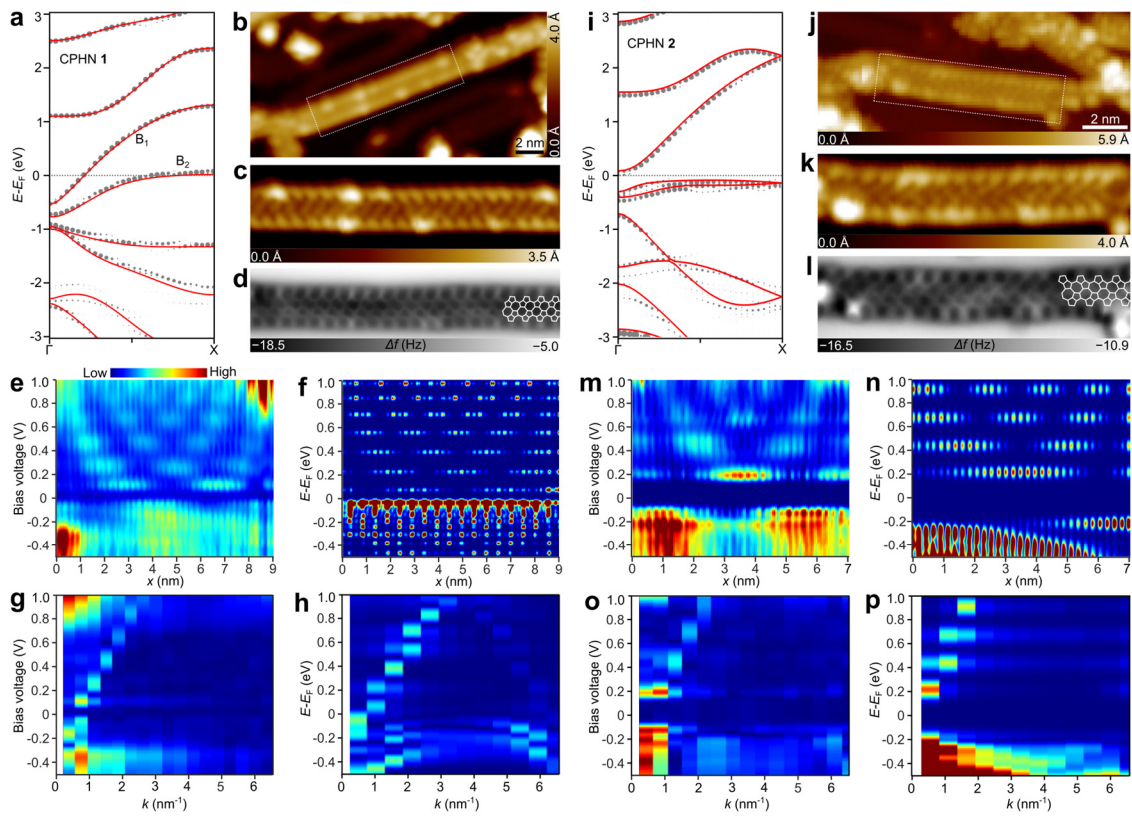
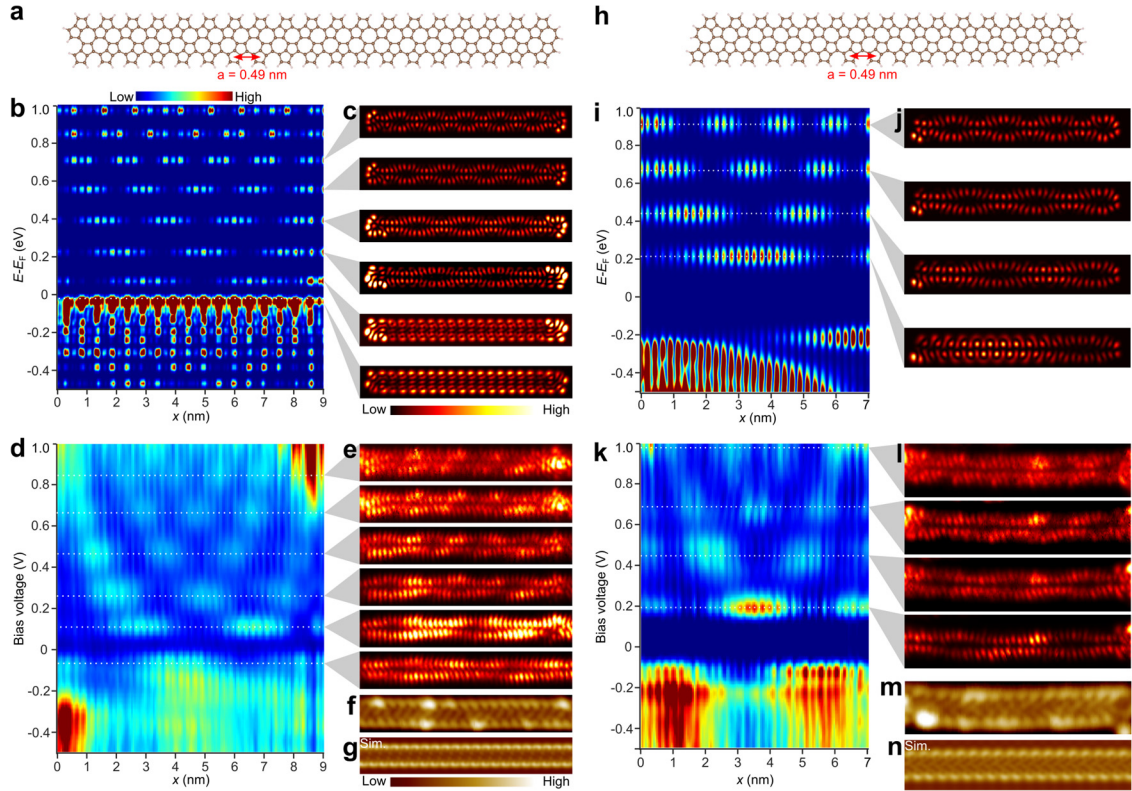
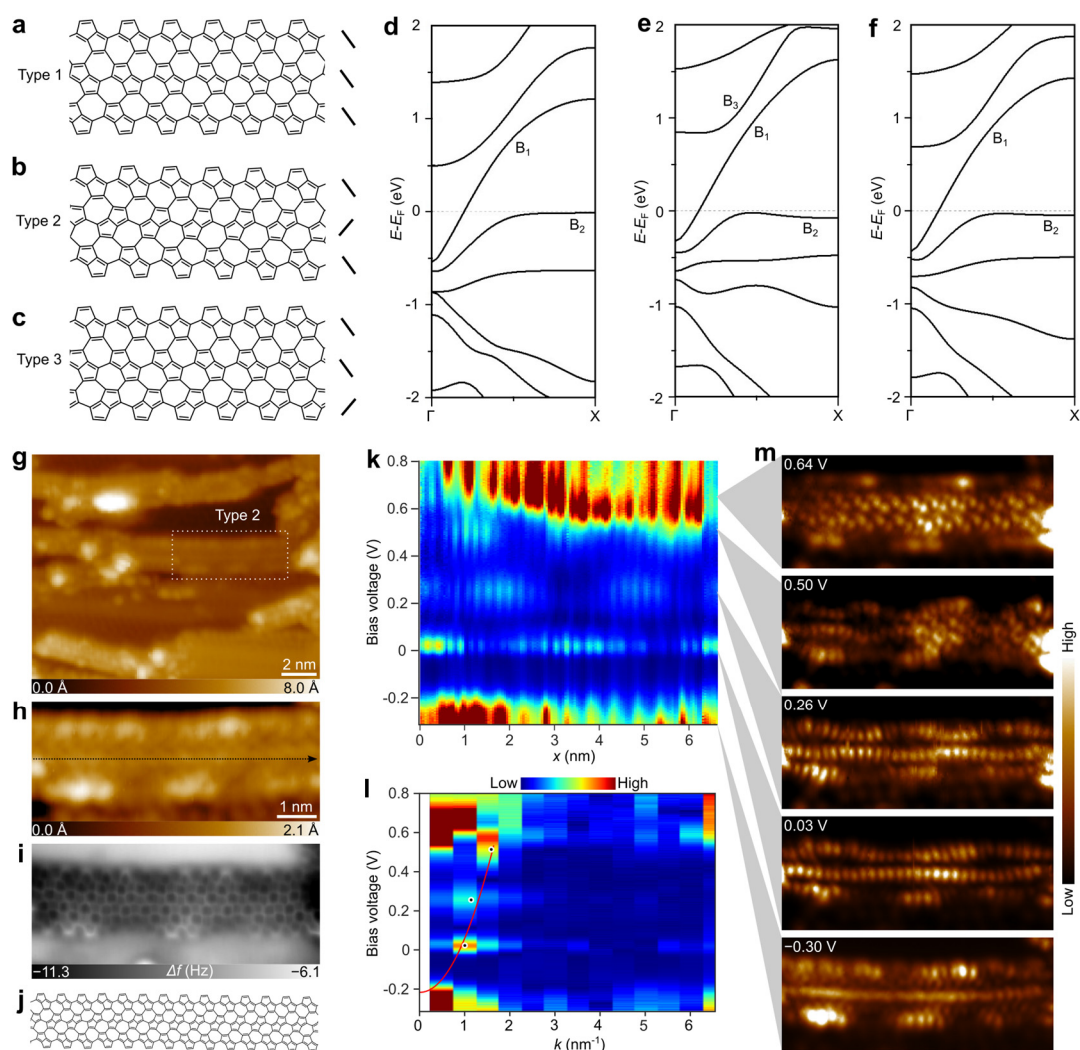


Fig. 4 | Electronic properties of CPHNs 1 and 2.



Extended Data Fig. 8 | Comparison of simulated LDOSs maps with experimental dI/dV measurements.



Extended Data Fig. 10 | Electronic properties of [3]CPHNs composed of three fused PPTLs.

8. How homogeneous/inhomogeneous is the Br intercalation? Based on Ext. Data Fig. 7a, it appears that segments of PPTL chains are also pushed upward by Br. What is the situation for the CPHN chains? Are they also partially intercalated? If so, what would be the reason?

Reply: In our experiment, we used a TBCO pressure of 10^{-8} mbar while maintaining the sample at 400 K to achieve Br intercalation. Under these conditions, all CPHNs were intercalated, while most PPTLs remained on the Ag(111) surface, except for some short PPTL chains covalently tethered to the CPHNs, as shown in **Supplementary Figs. 4e,f**.

As noted by the reviewer, some short PPTL segments were also lifted onto the Br layer, typically when directly connected to CPHNs. This suggests that the lifting of CPHNs facilitates the lifting of covalently linked PPTL segments. The easier lifting of CPHNs compared to PPTLs is primarily due to their weaker interaction with the Ag(111) surface. PPTLs contain antiaromatic pentalene units, which

tend to gain or lose two electrons for additional aromatic stabilization, making them more strongly bound to the surface.

To assess the homogeneity of Br intercalation under CPHNs, we recorded nc-AFM images of CPHNs **1** and **2** on the Br adlayer on Ag(111) using a CO-functionalized tip and compared them with nc-AFM images of CPHNs adsorbed directly on Ag(111), as shown by **Supplementary Fig. 16e**. The apparent height of CPHNs **1** and **2** on the Br adlayer in **Supplementary Fig. 16e** appears relatively flat, though not as uniform as on the Ag(111) surface (**Supplementary Fig. 16b**). Our results show that such slight inhomogeneity did not significantly affect QPI measurements to get the band structures, which are highly reproducible in DFT calculations. It is noticed that the relatively bright spot in STM images of CPHNs (**Fig. 4b,c** and **Fig. 4j,k**) can be inhomogeneous from defects in Br intercalation layer, since their AFM images (**Fig. 4d** and **Fig. 4l**) 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).

9. Supplementary Fig. 3 raises questions regarding the dI/dV spectroscopy (or the STM tips used for spectroscopy). The background spectra taken on Ag(111) do not exhibit the typical step-like surface state signal at around -65mV, but rather a peak at positive bias. Interpretation of the spectra acquired with such tip is very difficult.

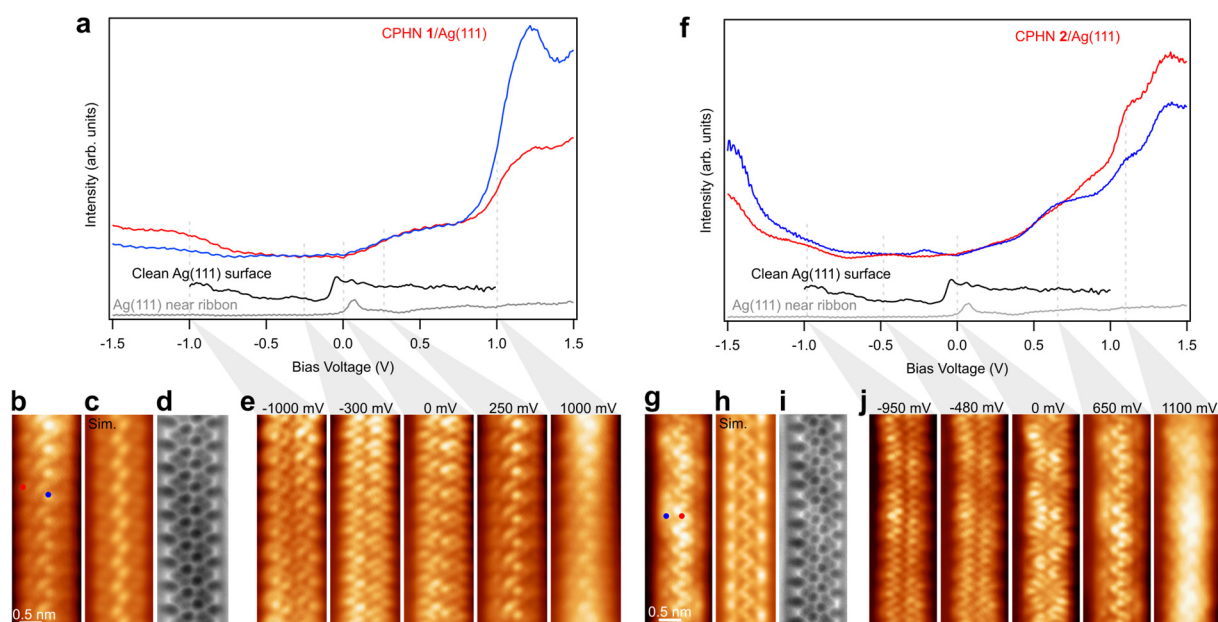
Reply: We thank the reviewer for highlighting this potentially confusing aspect.

We have confirmed that the background spectra taken on Ag(111) near CPHNs and PPTLs are correct. In such measurements, the coverage of the nanoribbons is quite high, resulting in only small bare areas of the Ag(111) surface (typically smaller than $5 \times 5 \text{ nm}^2$) available for recording the reference spectrum near the CPHNs. These bare surface regions, surrounded by the ribbons, lead to confined surface states of Ag(111) that shift to higher energies, consistent with previous studies [*J. Phys.: Condens. Matter* 2016, **28** 153003; *ACS Nano* 2022, 16, 16314–16321].

To avoid any ambiguity, we have labeled the background spectrum as “Ag(111) near ribbon” as shown in the revised **Supplementary Fig. 17**. In addition, a reference spectrum was recorded on a separate clean Ag(111) crystal without ribbons, both before and after the STS measurements on the CPHN/Ag(111) sample, to verify the tip condition. These reference spectra consistently exhibit the

characteristic step-like surface state at approximately -65 mV, as correctly noted by the Reviewer.

Additional description in the figure caption explaining the energy shifting of the Ag(111) reference spectrum obtained from the confined bare region of CPHN/Ag(111) sample is inserted, as: “The black and gray curves show the dI/dV spectra recorded on clean Ag(111) surface and bare Ag surface region in the CPHN/Ag(111) sample. 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.”



Supplementary Fig. 17 | STS measurements of CPHN 1 and 2 on Ag(111).

Referee #3 (Remarks to the Author):

The manuscript (MS) "Realising narrow carbon pentaheptite nanoribbons with strong metallicity" by Huang et al. reports on the on-surface synthesis of carbon nanoribbons composed solely of carbon pentagons and heptagons. The successful synthesis is verified using scanning tunneling microscopy (STM), noncontact atomic force microscopy (ncAFM) and tip-enhanced Raman spectroscopy (TERS). In addition, the authors performed extensive scanning tunneling spectroscopy to investigate the electronic properties of the pentaheptite GNRs and employed density functional theory to corroborate their experimental findings and shine light onto the reaction pathway of the nanoribbon formation.

The MS is mostly well-written, the data are of high quality, the experiments are overall extremely comprehensive, and the conclusions are supported by the data. The MS is very timely as advances in on-surface synthesis have led to a new surge of synthesizing novel carbon allotropes. Pentaheptite had been theoretically predicted around 30 years ago but its realization had remained elusive thus far. In addition to its successful synthesis, the authors demonstrate that a certain form of pentaheptite is metallic (as predicted), which is of note because graphene is semi-metallic and graphene nanoribbons are usually semi-conducting due to quantum confinement. Taking advantage of a skeletal rearrangement during the on-surface synthesis to transform cyclooctadiene into pentalene is another interesting detail, as – to the best of my knowledge – such a transformation had not been utilized yet for comparable on-surface synthesis pathways. It thus might open a route to the synthesis of other carbon (nano)structures.

Given the topic of the MS and the novelty of the results, this work should be of interest to chemists, physicists and material scientist alike, and I think the manuscript in principle is suitable for publication in Nature. However, there are a few comments I would like the authors to address before I can recommend its publication.

[Reply: We thank the reviewer's appreciation of our work.](#)

Comments:

Major:

1: Do the authors have ncAFM images of the PCOD chains? These would be of interest because of two points: (a) It is a bit surprising that Ullmann coupling appears to take place already at RT, because this usually requires slightly elevated temperatures on Ag(111), so it would be interesting to see whether this

interpretation is supported by ncAFM images. (b) It would be interesting to see the ncAFM images of the cyclooctadiene, to confirm that they have not yet transformed to pentalene.

Reply: We appreciate the reviewer's constructive suggestions.

We have performed nc-AFM imaging of the PCOD chains, as shown in **Fig. 1**. The images reveal that the COD moieties within the PCOD chains are highly nonplanar, with only the uppermost layer of carbon atoms visible in the constant-height nc-AFM mode. Consistent with previous observations, the nc-AFM images exhibit a periodicity of ~ 1 nm, which arises from the different adsorption configurations of adjacent COD units. Furthermore, the simulated nc-AFM images (**Fig. 1e**), based on the wavy topology of the PCOD structure (**Fig. 1f,g**), show good agreement with the experimental results.

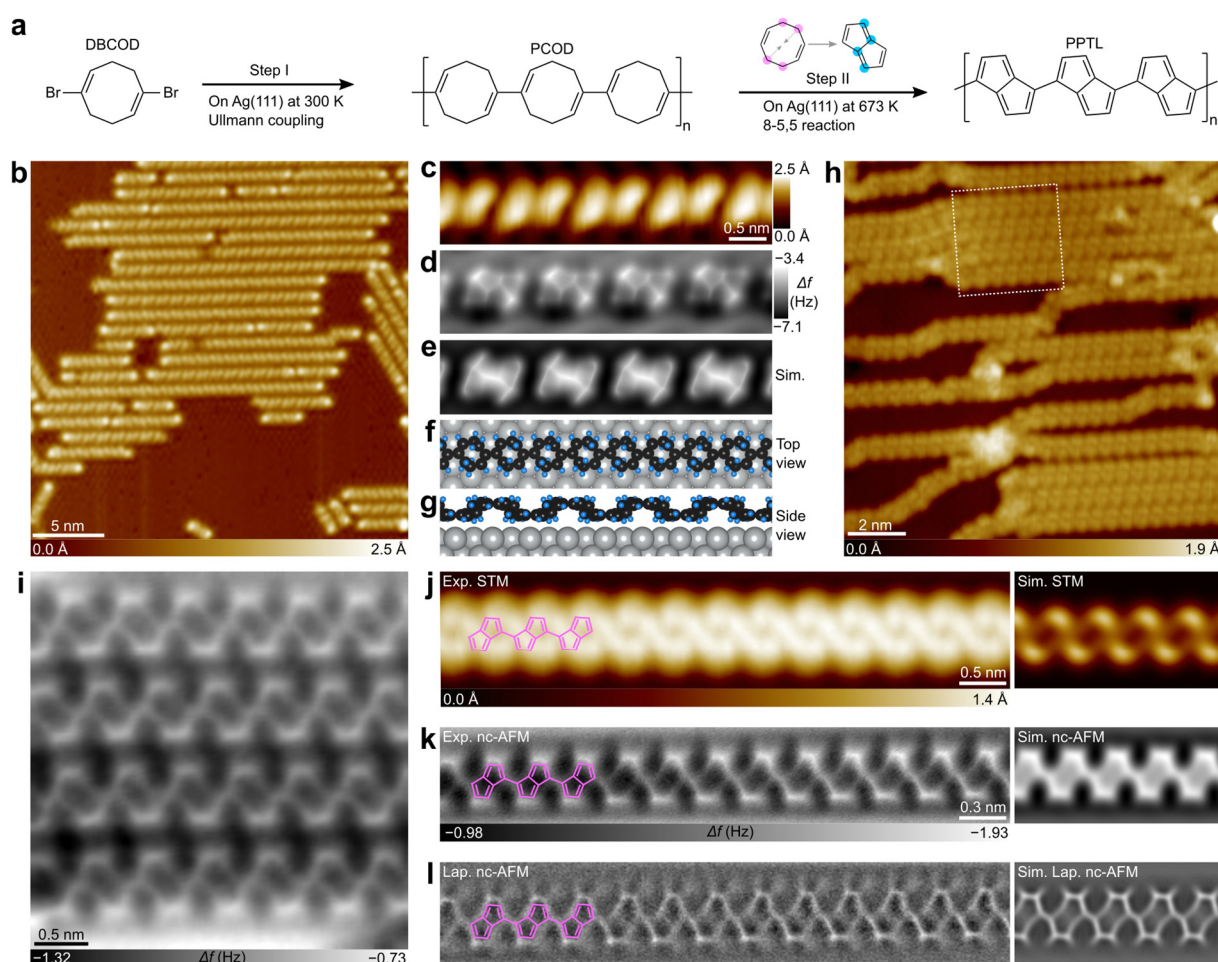


Fig. 1 | Characterization of the intermediates.

#2: Looking at the Fig. 1c, I am wondering if the same pentaheptite nanoribbons could be synthesized using directly a dibromo-pentalene precursor? Did the authors look into that?

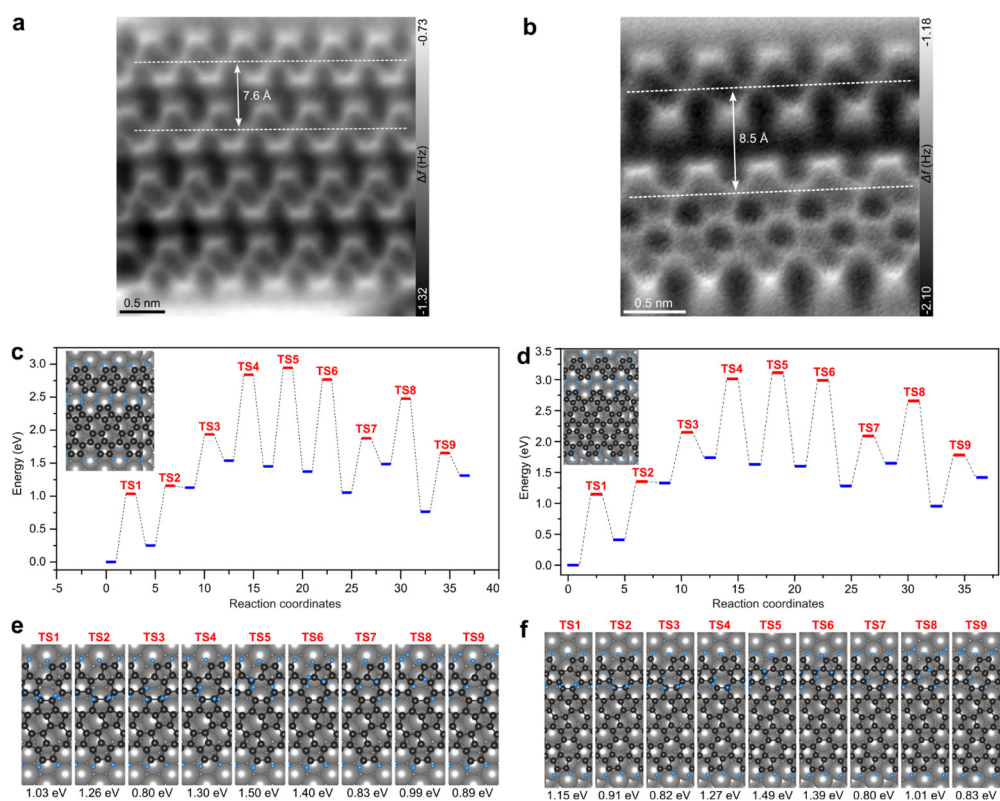
Reply: We appreciate the reviewer's constructive suggestion regarding an alternative approach to the synthesis of CPHNs. In the early stages of our research, we also proposed the use of a dibromo-pentalene precursor for CPHN synthesis. However, the inherent antiaromaticity of unsubstituted pentalene makes it highly unstable and dimerizes even at temperatures as low as $-100\text{ }^{\circ}\text{C}$ as reported in early work [*J. Am. Chem. Soc.* 1997, 119, 8, 1869–1875;]. This makes the synthesis of dibromo-pentalene substantially challenging. Consequently, we shifted our approach to using an octadiene precursor with an eight-membered ring carbon skeleton to directly generate pentalene on the surface in ultrahigh vacuum. This strategy also represents both the key innovation and the major advantage of our work.

#3: The authors state that the lateral growth/fusion would be self-limited, because they observe only rarely nanoribbons made from three PPTL chains. Could this also be due to the coverage or duration of the annealing? If the lateral growth should really be self-limiting, what would be reason for that?

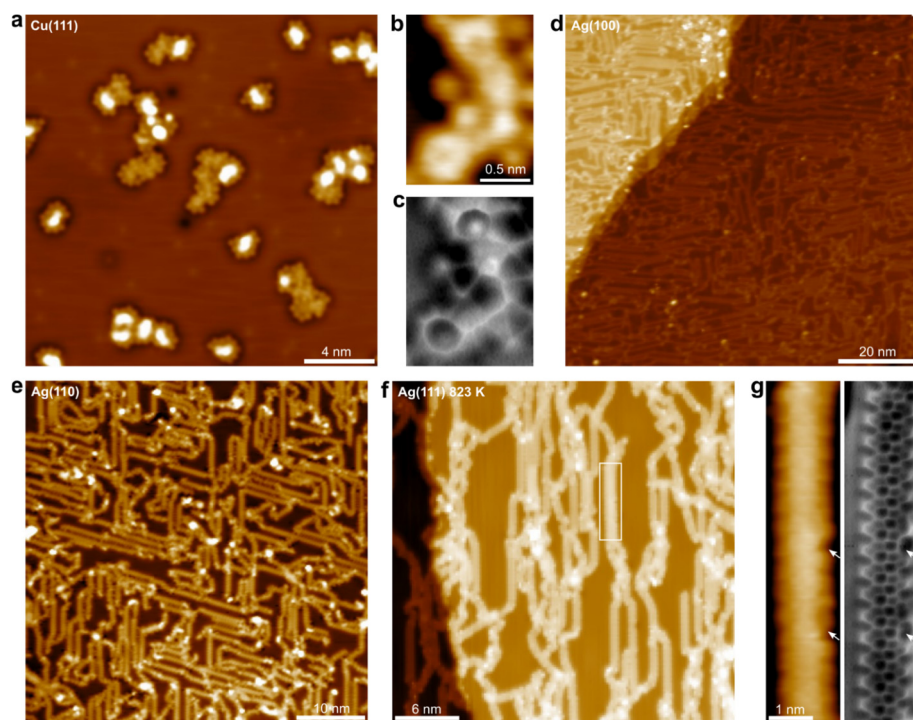
Reply: We have conducted additional CI-NEB calculations (**Supplementary Fig. 7**), which give a barrier of 1.5 eV for adding a PPTL chain to a CPHN **1**, just slightly larger than the barrier of 1.23 eV for the fusion of two PPTL chains. Note that these calculations have set the PPTL chain with the CPHN **1** spaced similar to the fusion of two PPTL chains (**Extended Data Fig. 3**). However, according to the observed possible initial structures before reaction (**Supplementary Fig. 7a,b**), there is relatively large separation between a PPTL chain and a formed CPHN **1** compared to two PPTL chains, which may be responsible for the lower yield of wider CPHNs due to their limited diffusion ability.

We have tried to anneal a full-coverage (PPTL formed by flattening of monolayer of PCOD, the bare surface area is spared out by the fusion reactions) sample at higher temperature (823 K) for extended durations as shown by **Supplementary Fig. 8f**. However, this leads to decomposition of the CPHNs structure 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 are also destabilized and destroyed.

The details of the optimization of the yield of CPHNs have been added into the **Supplementary Section 5**.



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



Supplementary Fig. 8 | Attempts of optimizing the synthesis of CPHNs using different surfaces and annealing temperatures.

#4: The agreement between the experimental TERS spectra and the calculated Raman modes is not great, both in terms of which modes are observed and their relative intensities. Could the authors please comment on that.

Reply: We acknowledge that our DFT calculations are based on freestanding CPHNs with infinite length, whereas our TERS experiments characterize finite-length CPHNs on a Ag(111) surface. The considerable charge transfer in the latter case may alter the vibrational frequencies. Additionally, the intensities of each peak in the TERS spectra are highly influenced by the plasmonic field between the tip and the surface. Therefore, to achieve a more accurate quantitative interpretation of the experimental TERS spectra, a systematic modeling of the CPHNs/Ag(111) adsorbate system, along with the tip-substrate picocavity, is necessary. We now have performed additional calculations by including the Ag(111) substrate and the plasmon field of the Pico cavity. The newly calculated TERS spectra are shown in **Fig. R1**, much better agreement has been achieved when compared to the experimental TERS spectra. However, due to the complexity of this physics behind, we choose to elucidate the TERS spectra of CPHNs in a separate work.

One of the most important factors cause the discrepancies is that the vibration modes are mainly in-plane, but the normal TERS measurements is not sensitive to the in-plane modes. While we have performed measurements using contact-mode TERS, the complexity in the contact-mode TERS still exists. To share our current progress at this point, we have performed additional calculations by including the Ag(111) substrate and the plasmon field of the Pico cavity. The newly calculated TERS spectra are shown in **Fig. R1** below, better agreement has been achieved when compared to the experimental TERS spectra. We find that the peak at 760 cm^{-1} can be acted as a fingerprint to distinguish the two types of CPHNs, where this peak is absent in CPHN **1**.

The simulated vibrational mode at 621 cm^{-1} (corresponding to the experimental mode of 644 cm^{-1}) in CPHN **1** (**Fig. R1c**) exhibits strong Raman intensity at the ribbon edges but is markedly weaker at the inner sites adjacent to the outer pentagon. This spatial dependence mirrors the experimental Raman spectra (**Fig. R1a**), where the 644 cm^{-1} peak diminishes from edge to center. By contrast, the 642 cm^{-1} mode in CPHN **2** (**Fig. R1d**) shows no discernible spatial variation, consistent with the uniform Raman

peak at 650 cm^{-1} (**Fig. R1a**). Distinct differences also emerge at higher frequencies: in CPHN **1**, coupled vibrations of the two PPTL chains give rise to modes at 829 and 835 cm^{-1} , matching the experimental peak at 823 cm^{-1} recorded at the ribbon center. In CPHN **2**, however, a 762 cm^{-1} mode corresponding to nearly independent chain vibrations is observed, with rather weak central intensity reflecting reduced interchain coupling, in agreement with the SSH ladder tight-binding model. Notably, CPHN **1** supports only a Raman-inactive interchain mode at 771 cm^{-1} in the $700\text{--}800\text{ cm}^{-1}$ range, explaining the absence of experimental features there. Thus, the 762 cm^{-1} mode serves as a fingerprint of CPHN **2**, absent in CPHN **1** owing to its stronger interchain coupling. Even though, the peak-to-peak agreement between the experimental and calculated results is still insufficient. Fortunately, the AFM images have already provided sufficient clear distinguishment by their structures between CPHN **1** and **2**.

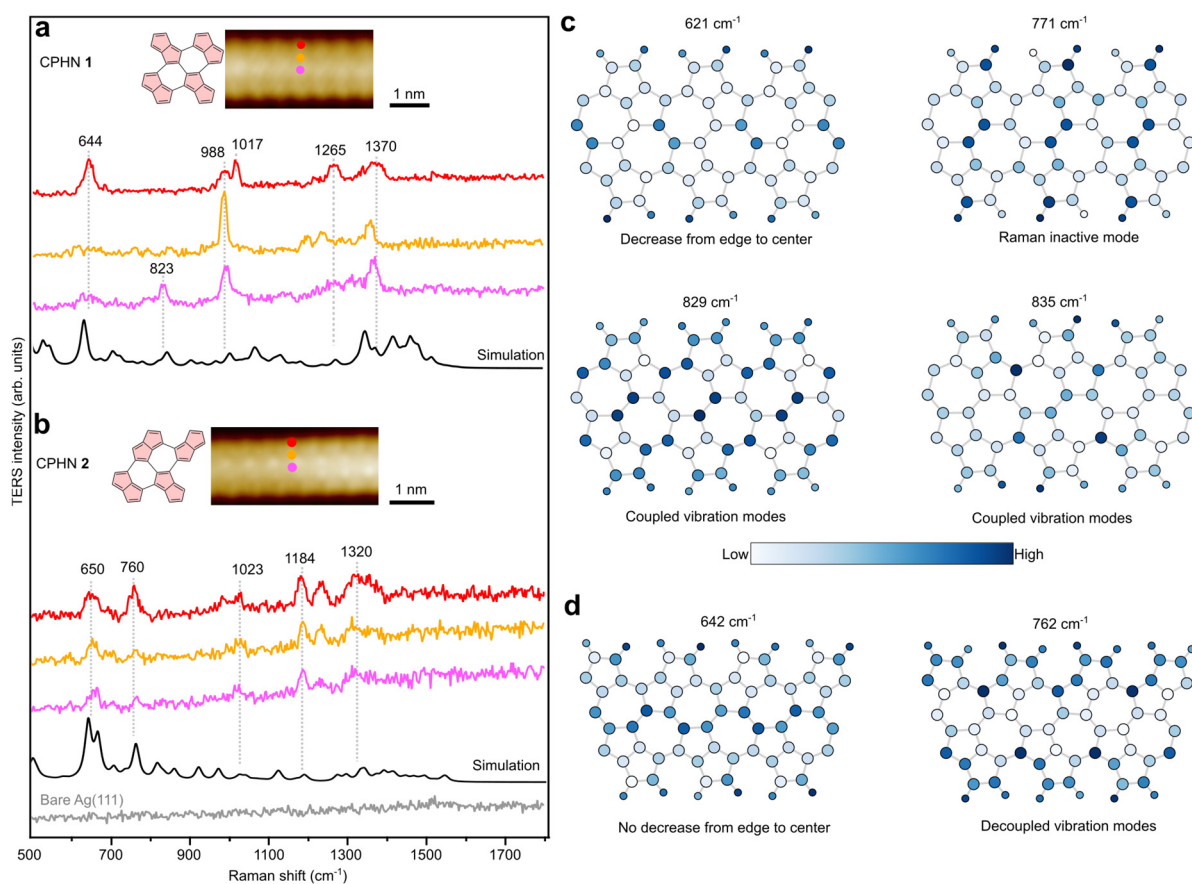


Fig. R1 | Vibrational modes of CPHNs. **a,b**, Tip-enhanced Raman spectra of CPHN **1** (**a**) and CPHN **2** (**b**) acquired in contact mode at the positions indicated by the correspondingly colored dots in the insets. For comparison, the simulated TERS spectra of CPHN **1** and CPHN **2** (shown in black) are also presented. **c,d**, The schematics of representative vibrational modes for CPHNs **1** (**c**) and **2** (**d**), respectively. The color intensity gradient of each atom reflects its contributions to the modulus of the

vibrational eigenvectors, i.e., the darker the color, the greater the atomic contribution to the vibrational mode.

#5 The experimental dI/dV maps in Ext. Data Figs. 8 and 9 are not very homogenous with significant intensity fluctuations along the lobes along the long ribbon axis. This is a bit surprising given that the ncAFM images show that the ribbons are of high quality with seemingly little to no defects. What is the origin of these fluctuations?

Reply: We appreciate the Reviewer's insightful comment. We have done additional experimental measurements and theoretical calculations. The results have been presented in **Fig. 4, Extended Data Figs. 8,9, and Supplementary Fig. 19**, which provide better agreement with the experimental observations from the QPI measurements. Additionally, longer CPHN **1** and CPHN **2** are also calculated (**Supplementary Fig. 20**). These results provide solid support for our claims that CPHN **1** exhibits strong metallicity and CPHN **2** functions as a narrow bandgap semiconductor.

Using QPI measurements and simulations, we have identified that the observed intensity fluctuation is actually quantum well states along the ribbons (**Fig. 4**), which have been used to measure the band structure, and provided compelling evidence for metallic CPHN **1** and CPHN **2**, of the major topic of this work.

#6: Somewhat related to #5: Can the authors exclude other origins of the peak close to zero energy for the CPHN 2 ribbons? E.g., due to magnetism (Kondo effect), in particular because the spectra in Ext. Data Fig. 8c also show some bias-symmetric steps around +/- minus 100 mV, which could also be interpreted as being due to inelastic tunneling processes such as spin flips.

Reply: We appreciate the reviewer for bringing up this issue. Similar comments were also raised by Reviewer 2.

We have conducted additional experiments and theoretical calculations and analysis for better understanding of the nature of the zero-bias peak observed in the chains of CPHN **1**, and have compared with the additional results from CPHN **2** and PPTL.

There is a van Hove singularity (vHS) due to the existence of band extrema near the E_F , as shown

in **Figs. 3,4**. However, it is now clear that the previously observed zero-bias peak in the CPHN **1** should not be contributed by the vHS. Instead, the presence of the zero-bias peak in the CPHN **1** can be attributed to the occasional location of the metallic band minimum at the E_F (**Extended Data Fig. 9d**), which is found to depend on the length of CPHN **1**, as well as the sites measured along the ribbon. In addition, our spin-polarized DFT calculations show that magnetism of CPHN **1** and **2** on Br/Ag(111) should be negligible (**Extended Data Fig. 5**). These observations can largely exclude the possible effects from Kondo resonance or other inelastic effects.

Minor:

#7: Abbreviation PCOD is not defined, I think.

Reply: We thank the reviewer's comments. We now defined PCOD in the main text.

#8: l. 107: Is TTPL a typo and should be PPTL?

Reply: We thank the reviewer's comments. This issue has been addressed.

#9: Ext. Data Fig. 7: Panel a and b have labels named PHCN. Should those be CPHN?

Reply: We thank the reviewer's comments. This issue has been also pointed out by reviewer 1 and has been addressed accordingly.

#10: l. 231 ff.: "[...], and may be beneficial to the suppressed instability caused by the open-shell characteristics that commonly exist in narrow GNRs with pure hexagonal rings." I am not sure whether I understand that statement. Maybe it could be reformulated to make its meaning more clear?

Reply: We thank the reviewer's comments. To enhance the readability of this sentence, we revised the description into:

"Narrow CPHNs composed solely of 5-7 rings may inherit the stability of their 2D counterparts, and could help mitigate the instability typically associated with the open-shell characteristics of narrow GNRs composed of pure hexagonal rings"

Point-by-point response to Referees' comments:

Referee #2 (Remarks to the Author):

Report on MS (2024-06-11486B-Z) "Narrow carbon pentaheptite nanoribbons as a covalent metal" by J. Huang et al.

The manuscript by Bing Wang and co-workers reports the on-surface synthesis of carbon pentaheptite nanoribbons (CPHNs). The authors first achieve the formation of polypentalene (PPTL) chains, followed by a lateral fusion process leading to the target CPHNs. Two structural variants are formed, denoted CPHN1 and CPHN2. Both structures consist exclusively of five- and seven-membered rings but differ in the relative orientation of the fused PPTL chains: in CPHN1, the pentalene units of the two PPTL chains have the same orientation, whereas in CPHN2 the orientations are opposite. This structural difference leads to distinct space-group symmetries ($P2/m$ for CPHN1 and nonsymmorphic $Pmc2_1$ for CPHN2) and motivates the electronic distinctions discussed in the manuscript. The theoretical analysis supporting this distinction is twofold. Density functional theory (DFT) calculations demonstrate that CPHN1 exhibits overlapping bands and metallic behaviour, while CPHN2 shows a small bandgap and semiconducting character. The extended SSH tight-binding model introduced in the revised version provides the physical explanation for these DFT results. It identifies how the symmetry imposed by the PPTL orientations controls the allowed inter-chain hopping amplitudes and either lifts the degeneracy at the X-point (CPHN1, metallic) or enforces a degeneracy leading to flat bands near E_F and a finite bandgap (CPHN2). Thus, the reported electronic differences arise from a combination of DFT band-structure modelling and tight-binding symmetry analysis.

The authors further perform tip-contact transport and STM/STS measurements to probe the electronic properties of the CPHNs. Additionally, Br-intercalation is employed to decouple the nanoribbons from the substrate and reveal their intrinsic electronic characteristics. In the revised version of the manuscript, the main modifications include the removal of the poorly matched TERS data, the addition of quasi-one-dimensional QPI measurements (Fourier-transformed dI/dV line profiles), and the use of an extended SSH model to discuss the origin of metallic and insulating properties of the two CPHN variants.

[Reply: We thank the reviewer for the careful reading and evaluation of the revised manuscript.](#)

In my opinion, the low quality and yield of the target products remain a major limitation. The synthesis pathway inherently leads to high defect density. The resulting structures display numerous junctions, bending, distortions, and various fusion motifs. The overall sample

morphology resembles a disordered two-dimensional network with random connections between PPTL and CPHN segments, rather than well-defined nanoribbons. Only short CPHN segments are found and studied. This strongly restricts reproducibility and systematic investigation.

Reply:

We appreciate the referee's concern regarding the overall yield and the apparent structural complexity of the as-prepared samples. We agree that the yield of the target CPHN products ($\sim 18\%$ in our statistics) is lower than in some established on-surface nanoribbon syntheses. However, our central point is that the structural quality and availability of defect-free CPHN segments are fully sufficient and in practice reliably attainable for rigorous electronic characterization by STS/QPI and for transport measurements.

First, while junctions and terminal fusion events do occur, we routinely resolve well-defined, defect-free CPHN backbones with lengths more than 10 nm (>20 -unit cells). Importantly, the imperfections are predominantly associated with ribbon termini (e.g., end-to-end tethering or occasional terminal fusion motifs), whereas extended interior segments maintain a uniform ribbon structure. These defect-free segments provide a robust experimental basis for extracting intrinsic electronic properties.

Second, we acknowledge that at high coverage the samples can visually resemble a partially connected network due to covalent tethering between ribbon termini. This morphology reflects inter-ribbon end connectivity rather than a loss of structural definition along the ribbon backbone. Crucially, even when ribbon ends are tethered, individual CPHN segments remain clearly identifiable and electronically well-defined over extended lengths, allowing reproducible spectroscopy on the same structural motif across many segments. The disordered/defective structures arising from covalent tethering at the termini of otherwise well-defined CPHN segments mainly serve as effective scattering centers, enabling clear QPI measurements without compromising the ribbon backbone.

Most importantly, our conclusions do not rely on subjective assessments of morphology but on direct electronic readouts that intrinsically require high structural integrity. In particular, the observation of clear standing-wave patterns and well-defined dispersions in QPI demands sufficiently long, low-defect, quasi-1D segments; the fact that we repeatedly obtain these QPI signatures demonstrates that the accessible CPHN segments are of adequate quality for advanced band-structure determination. Consistently, our transport measurements further corroborate that the relevant ribbon segments support coherent conduction behavior compatible with the extracted electronic structure.

Finally, although the yield is not yet optimal, STM-based characterization and device fabrication are inherently segment-selective: an $\sim 18\%$ yield is practically sufficient to locate

multiple defect-free CPHN segments per sample and to perform systematic STS/QPI and transport studies. We therefore view the current synthesis as already enabling a high-feasibility experimental platform. The key outcome of this work is the identification and verification of an intrinsically metallic narrow nanoribbon and its experimentally accessible band structure, which opens realistic opportunities for probing one-dimensional correlated phenomena and transport in a chemically well-defined metallic carbon-based system.

Compared with the established design of metallic graphene nanoribbons (Science 369, 1597–1603, 2020), the current approach seems significantly more difficult to reproduce or extend. Since the metallic behavior reported here is not an emergent phenomenon but a property relevant for applications, I believe that addressing the present synthetic limitations is essential.

Reply:

We thank the referee for highlighting the importance of synthetic reproducibility and scalability, particularly because the metallic behavior reported here is intrinsic to the ribbon electronic structure rather than an emergent, condition-dependent phenomenon. We fully agree that improving synthetic control and yield will be essential for future technological translation.

At the same time, we emphasize that the present work targets an unusually challenging structural motif: the CPHNs realized here represent, to our knowledge, the first atomically precise narrow nanoribbons built entirely from non-hexagonal (5/7) carbon rings. Accessing such a fully non-benzenoid backbone necessarily requires a non-standard reaction design beyond established “Ullmann coupling + cyclodehydrogenation” paradigms. The resulting synthetic pathway is therefore less conventional and currently offers less straightforward tunability than more established routes; this is an inherent trade-off at the present stage of creating a qualitatively new nanoribbon topology.

Importantly, despite these current limitations, our synthesis already provides a practically reproducible experimental platform for determining intrinsic electronic properties. The as-prepared samples routinely contain well-defined, sufficiently long CPHN segments that enable (i) robust STS/QPI measurements resolving the metallic dispersion and (ii) successful transport characterization. Moreover, the Br-assisted decoupling strategy introduced here further stabilizes and electronically isolates the ribbons, which is critical for reproducibly accessing the intrinsic metallic band structure by QPI and for enabling reliable electrical probing. In this sense, while yield and large-scale uniformity remain open directions, the current approach already allows the community to systematically investigate an intrinsically metallic, fully 5/7-ring nanoribbon using state-of-the-art local spectroscopy and transport methods.

Finally, regarding applications: we have revised the manuscript to clarify that our discussion of

“conductive carbon nanowires” is intended strictly as a prototype-level perspective and an outlook motivated by the experimentally observed high conductance. We do not claim immediate device readiness; rather, we present the intrinsic metallic CPHN as a new material platform whose unique topology and robust metallicity make it promising for future one-dimensional correlated-physics studies and, in the longer term, potential carbon-based interconnect concepts once synthetic control, handling, and integration are further developed.

The electronic properties of the synthesized structures also remain insufficiently clarified. In the STS measurements, CPHN **1** segments exhibit either insulating or metallic behavior depending on the alignment of the Fermi level with discrete quantum well states. In this situation, the consistent appearance of a robust zero-bias peak in the contact transport measurements is unexpected and requires clearer explanation. Simply omitting this discrepancy from the main figures does not resolve the issue.

Reply:

We thank the referee for this important comment and agree that the electronic properties and the relation between STS and contact transport require a clearer explanation. We would like to clarify that, for a finite-length 1D conductor, the electronic spectrum is necessarily discretized into quantum-well states (QWS) by confinement, and therefore a state does not have to fall exactly at E_F for the system to be metallic. The criterion “metallic = an eigenstate exactly at E_F ” is not the standard definition and would incorrectly classify many well-known finite 1D metallic systems such as carbon nanotubes and atomic chains [see references; L. C. Venema *et al.*, *Science* **283**, 52–55 (1999); J. Lee *et al.*, *Phys. Rev. Lett.* **93**, 166403 (2004); T. F. Mocking *et al.*, *Nat. Commun.* **4**, 2387 (2013); N. Oncel *et al.*, *Phys. Rev. Lett.* **95**, 116801 (2005)] as “insulating” simply due to an accidental level alignment. In a finite segment derived from a metallic 1D band, the QWS energies sample the underlying dispersion; depending on the chain length and boundary conditions, E_F can lie on a QWS peak or between two adjacent QWS peaks (an expected even–odd/length-dependent effect). This produces a finite-size level spacing $\delta E \sim \pi \hbar v_F / L$, i.e., a quantization gap that scales to zero as $L \rightarrow \infty$, and should not be confused with a true insulating band gap that remains finite in the thermodynamic limit. Importantly, in our QPI/QWS analysis the extracted dispersion crosses E_F (equivalently, the series of QWS spans energies on both sides of E_F), demonstrating that the parent infinite system is gapless/partially filled. Moreover, experimental broadening (instrumental resolution and thermal broadening) provides finite spectral weight at E_F even when E_F lies between two discrete QWS maxima. Therefore, the observation that E_F sometimes falls between adjacent QWS peaks is a finite-size quantization effect, not evidence of an insulating state, and it is fully consistent with a metallic 1D band in the long-chain limit.

Concerning the robust zero-bias peak in the contact (lifting) transport measurements, we

performed additional DFT-based transport calculations and found that the lifting/contact geometry induces charge transfer and Fermi-level pinning as suggested by the referee, which aligns one QWS with E_F and thus produces the consistent zero-bias feature. We have now explicitly included this mechanism and the supporting results in the revised manuscript (and corresponding figures), rather than omitting the discussion.

Moreover, we have performed additional AFM, STS, and transport measurements using different samples of CPHN **1** (see below in reply to the comment #3 and Supplementary Figs. 11, 23, 24). The transport measurements give similar behaviors with zero-bias peak, whereas, either at the free ends or connectors, the site-dependent dI/dV spectra do not show zero-bias peak. These additional experimental results can largely exclude the possibility of Kondo effects from end-state or defect-state spins. Referee pointed out that “*the consistent appearance a robust zero-bias peak in the contact transport measurements is unexpected*”. On the basis of transport calculations, we have now clarified that the Fermi-level pinning of a quantum well state (QWS) derived from metallic band B_1 contribute to the robust zero-bias peak in the contact transport measurements. We believe our results do reflect its uniquely intrinsic property, in agreement with the band structure and transport property from our theoretical calculations.

In the revised manuscript, we have added these results in Supplementary Fig. 18 and Supplementary Section 9. In the main text, we have put back the results in Fig. 2, and added a paragraph, it reads “Our transport calculations for CPHN **1** adsorbed on two Ag electrodes (Supplementary Fig. 18 and Supplementary Section 9) reveal a zero-bias transmission state arising from Fermi-level pinning [You, S. *et al.* Quantifying the conductivity of a single polyene chain by lifting with an STM tip. *Nat. Commun.* **15**, 6475 (2024).] of a quantum well state (QWS) derived from metallic band B_1 , whose wavefunction spreads over the CPHN **1**. The electron transfer from the electrodes to CPHN **1**, as observed for CPHN **1** on bare Ag in Extended Data Fig. 6b, may facilitate the Fermi-level pinning. This Fermi-level pinning can explain the zero-bias differential conductance peaks observed experimentally in various CPHN **1** samples (Fig. 2i, Supplementary Figs. 9i,j and 11f).”

Detailed questions/comments:

For sample growth

1. The statistical analysis of the reported 21.8% CPHN yield appears overly simplistic and lacks methodological rigor. As shown in Supplementary Figures 4 and 5, many of the observed products display unclear structures with numerous junctions, bending, distortions, and structural irregularities. Despite this, the authors classify all such defective structures as either CPHN or PPTL, which likely leads to a substantial overestimation of the actual yield.

Reply:

We agree with the referee that the statistical treatment of the CPHN yield should be described with greater methodological rigor, particularly given the presence of junctions, bending, and ill-defined motifs in some regions of the STM images. In our CPHN sample, well-defined CPHNs and PPTLs are indeed the dominant products, while a smaller fraction of structurally ambiguous/defective species (e.g., junctioned or strongly distorted segments) is also present.

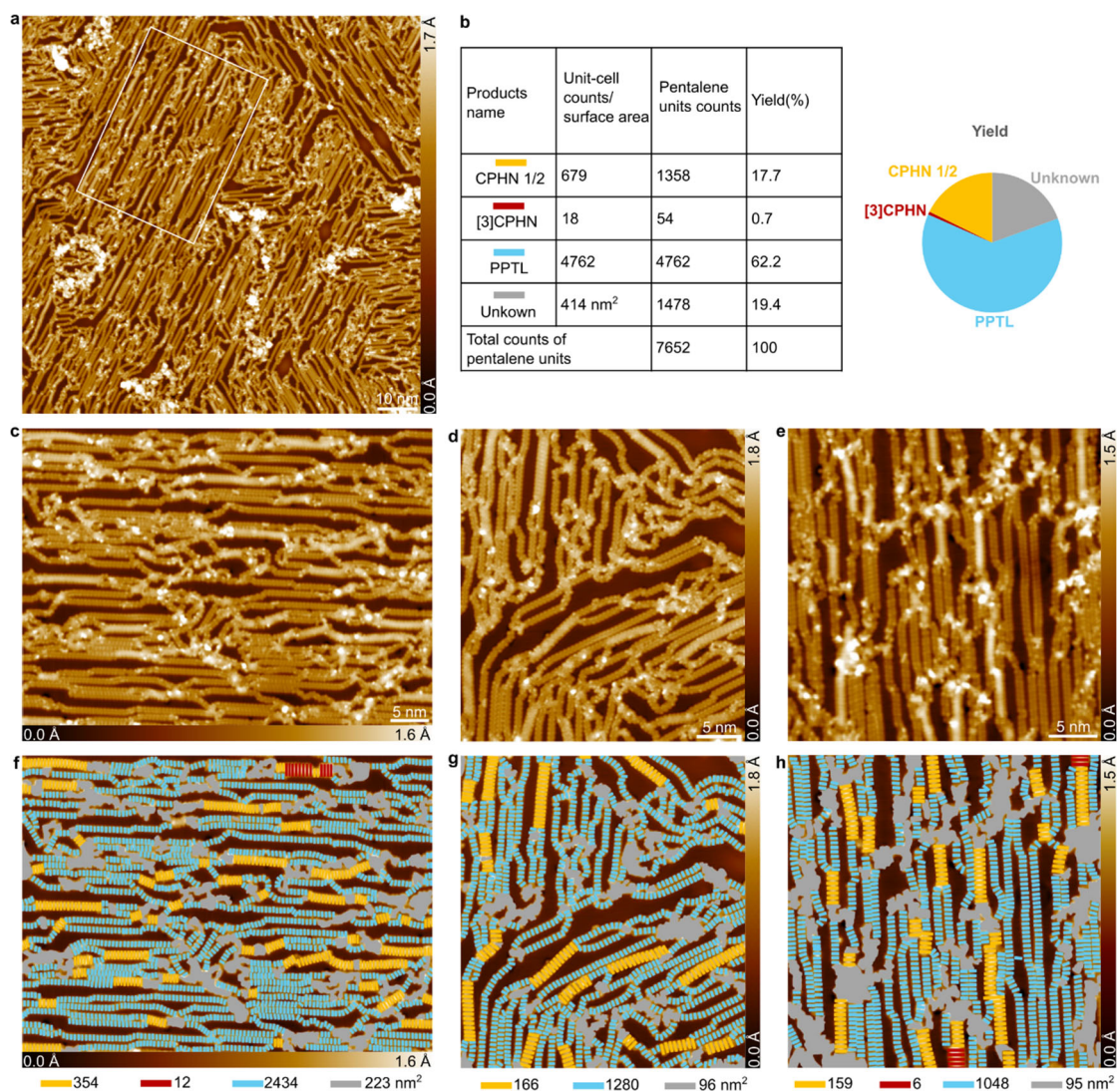
In the revised manuscript, we have re-evaluated the yield using a more explicit and conservative workflow and clarified all counting criteria in Supplementary Fig. 4 (and Supplementary Fig. 5). Importantly, we do not force-assign structurally irregular regions as either CPHN or PPTL. Specifically, the CPHNs yield is defined on the basis of pentalene repeat units as

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

Here, $N_{\text{CPHN } 1/2}$, $N_{[3]\text{CPHN}}$, and N_{PPTL} are obtained by directly counting the numbers of pentalene units assigned to well-resolved CPHNs (yellow sticks for CPHN **1/2** and red sticks for [3]CPHN) and PPTL (cyan sticks), respectively (values summarized in the table in Supplementary Fig. 4b). Regions exhibiting junctions, severe distortions, or unclear motifs are categorized separately as “unknown/disordered” (gray-shaded regions) and contribute to N_{Unknown} rather than being classified as CPHN or PPTL.

To estimate N_{Unknown} in a reproducible manner, we convert the gray-shaded area into an equivalent pentalene-unit count using an areal pentalene density of 3.57 pentalene nm⁻². This density is calibrated from the same dataset under identical imaging conditions (Supplementary Fig. 4g), where 332 pentalene units occupy an area of ~93 nm² covered by clearly resolved CPHNs. We also explicitly account for the different repeat-unit compositions, i.e., one CPHN **1/2** repeat unit (yellow) contains two pentalene units and one [3]CPHN repeat unit (red) contains three pentalene units.

Based on the statistical analysis of three independent STM areas (Supplementary Fig. 4c–e), the overall CPHN yield is 18.4% (~17.7% CPHN **1/2** and ~0.7% [3]CPHN). Compared to the previously reported value, this updated yield is slightly lower and reflects the more conservative treatment of ambiguous/defective regions. We have added annotated images (Supplementary Fig. 4f–h) and the full counting procedure in the figure caption to ensure transparency and reproducibility.



Supplementary Fig. 4 | Statistical analysis of CPHN yields.

2. On page 6, lines 19–20, the authors attribute the lower yield of wider CPHNs to “the increased separation of the formed CPHNs from a neighboring PPTL chain (Supplementary Fig. 7a).” However, the experimental observations suggest an alternative explanation. The extensive joint fusions, bending, and distortions within the network likely suppress the lateral mobility of all nanoribbons, thereby reducing the yield of wider fused structures. Moreover, the theoretical calculations used to support the proposed mechanism rely on idealized, isolated, straight ribbon models, which do not reflect the structural disorder observed experimentally. I note that Reviewer 3 already raised this issue in the first round (comment #3), and it remains unresolved.

Reply:

We thank the referee for this important point and agree that our previous wording (“the increased separation of the formed CPHNs from a neighboring PPTL chain”) was overly simplified and could be interpreted as implying that the increased spacing is the only reason

why wider CPHNs are obtained with lower yield. This was not our intention, and we have revised the text accordingly.

Experimentally, during lateral fusion we indeed observe that once a CPHN segment forms, its termini can become tethered to nearby, not-yet-fused PPTL segments (or other ribbons). Such tethering, together with the joint fusions, bending, and distortions in the crowded network, can suppress the lateral mobility of the nanoribbon ensemble. We agree with the referee that this mobility reduction is a realistic and relevant factor that hinders subsequent fusion events needed to grow wider fused structures.

At the same time, the formation of wider CPHNs does not exclusively occur after a CPHN has already become tethered. We also observe dense PPTL “islands” (e.g., Fig. 1h, Supplementary Fig. 6) that are mobile upon heating up to the fusion temperature and can undergo fusion simultaneously while still in a relatively dynamic state. Nevertheless, even in these regions, the fusion process progressively reduces the local packing density: after some ribbons fuse, the remaining neighboring PPTL chains become more sparsely distributed than in the initial dense PPTL islands. Consequently, further lateral fusion events required to form wider ribbons become less probable simply because suitable partners are less frequently encountered.

Regarding theory, we fully acknowledge that our calculations employ idealized, isolated, straight ribbon models and therefore do not explicitly account for tethering-induced mobility suppression or the structural disorder observed experimentally. In practice, the mobility reduction associated with tethering formation is difficult to quantify computationally in a rigorous manner within our current framework. Our calculations are therefore not intended to reproduce the full disordered morphology, but rather to provide mechanistic insight into the intrinsic reactivity of the fusion step: specifically, when mobility effects are not considered, the calculated barriers for PPTL–PPTL fusion and PPTL–CPHN fusion are comparable. This implies that the experimentally observed difference in yield for wider CPHNs is unlikely to originate from a fundamentally higher chemical barrier for PPTL–CPHN fusion, but instead is dominated by kinetic limitations. Namely, (i) the increased effective spacing between ribbons after fusion proceeds and (ii) the reduced mobility caused by tethering and network-like constraints. We have clarified this interpretation in the revised manuscript and adjusted the text to explicitly state that both effects contribute:

“The lower yield of wider CPHNs likely results from a reduced probability of further lateral fusion, due to both (i) the increased separation between newly formed CPHNs and nearby PPTL chains (Supplementary Fig. 7b) and (ii) tethering/network constraints that suppress nanoribbon mobility.”

For electronic properties

3. My main concern is the discrepancy between the QPI and contact transport measurements for CPHNs. The QPI patterns clearly reveal quantization of the dispersive band, with 0.1–0.2 eV gaps between discrete levels depending on ribbon length. This indicates that the metallic or insulating behavior of short CPHN ribbons depends on whether the Fermi level aligns with a discrete energy level or falls within a gap, both of which are observed in the STS data (ED-Fig. 7 and ED-Fig. 9). In contrast, the contact transport measurements for CPHN1 consistently exhibit a strong zero-bias peak. Given that the authors employ an extended SSH model, the question arises whether this zero-bias anomaly could originate from a topological end mode or another mechanism intrinsic to the model. An alternative explanation that should be considered is the pinning of one of the discrete quantum well states, plausibly the first valence or conduction band state, to the Fermi level of the tip or sample, which could also give rise to a robust zero-bias feature. This requires clarification.

Reply: We appreciate the referee for the insightful comments.

We are grateful to the referee for the suggestion about *the pinning of one of the discrete quantum well states*. After carefully consider this suggestion, we have performed transport calculations. The calculated results show that the robust zero-bias differential conductance peak arises from the Fermi-pinning of a QWS state, which is evidence by the pronounced zero-bias transmission peak. The calculated transport results are in good agreement with the QPI patterns that frequently show the Fermi level aligning with a discrete energy level. We believe that in the transport measurements, the contact of the electrodes may further facilitate this alignment, which is somewhat different from the QPI measurements that are performed using Br-decoupled CPHNs. In the calculations, we modelled CPHN 1 adsorbed on two Ag electrodes for simplicity, which could be reasonable by considering the similar work functions between Ag and W.

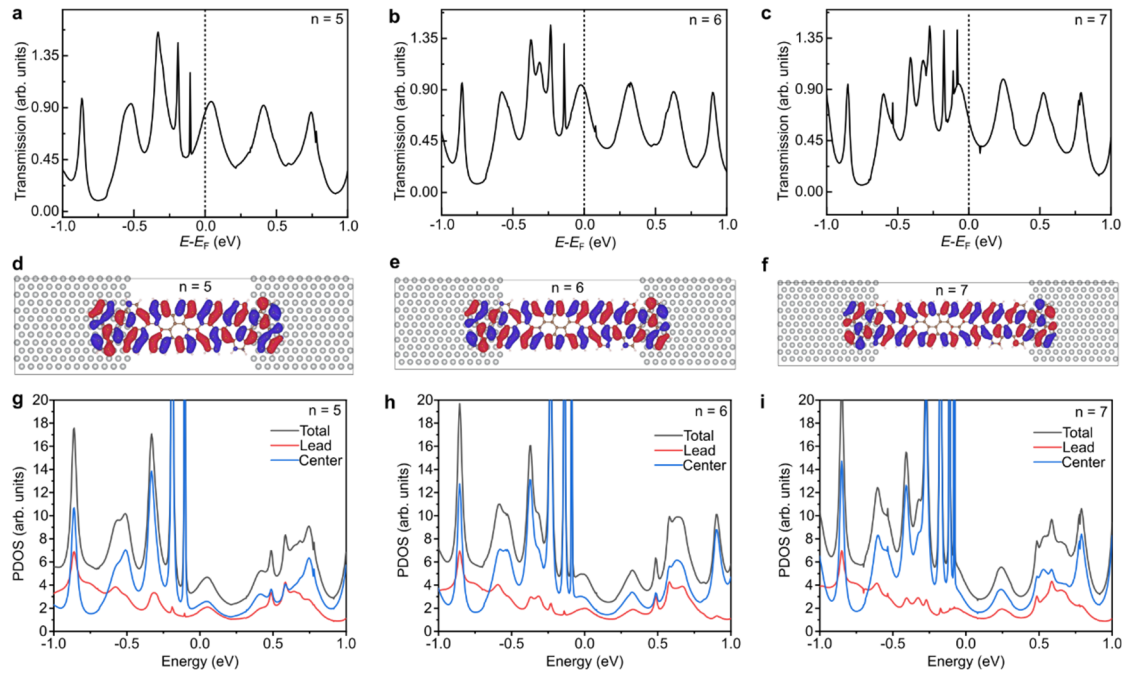
We further performed combined transport and local spectroscopy on the same CPHN 1 ribbon on Ag(111) (Supplementary Fig. 11). The lifting experiment again yields a high conductance of $\sim 0.4\text{--}0.8 G_0$ for tip heights of 1–5 nm (Supplementary Fig. 11d), and the corresponding I – V and dI/dV curves show a strong enhancement near zero bias (Supplementary Fig. 11e,f), consistent with the two-electrode calculations. In the measurements, we find that end-site STS does not show a zero-energy end peak (e.g., no Kondo-like resonance pinned at E_F) at the terminus (Supplementary Fig. 11j,k), which can largely exclude the possible Kondo effect from defect-induced localized spin states at the ribbon ends. Moreover, the real-space dI/dV maps do not reveal a terminus-only state; instead, the ribbon interior exhibits prominent spectral weight across the near- E_F energy window (approximately –130 meV to 140 meV; Supplementary Fig. 11i), again inconsistent with a sharply localized mid-gap boundary mode.

However, though the robust appearance of the zero-bias peak in the transport measurement, the peak is relatively narrow, which can be rationalized by considering a less aligned QWS state with the Fermi level.

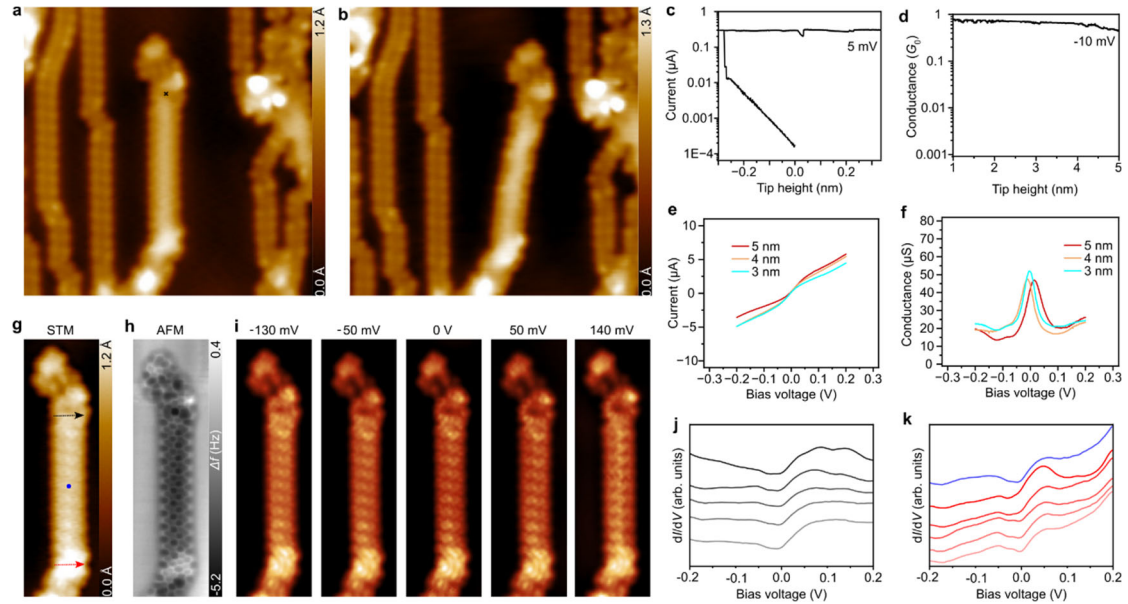
In the main text, we have included the explanation about the origin of the robust zero-bias peak, it reads “Our transport calculations for CPHN **1** adsorbed on two Ag electrodes (Supplementary Fig. 18 and Supplementary Section 9) reveal a zero-bias transmission state arising from Fermi-level pinning [You, S. *et al.* Quantifying the conductivity of a single polyene chain by lifting with an STM tip. *Nat. Commun.* **15**, 6475 (2024).] of a quantum well state (QWS) derived from metallic band B₁, whose wavefunction spreads over the CPHN **1**. The electron transfer from the electrodes to CPHN **1**, as observed for CPHN **1** on bare Ag in Extended Data Fig. 6b, may facilitate the Fermi-level pinning. This Fermi-level pinning can explain the zero-bias differential conductance peaks observed experimentally in various CPHN **1** samples (Fig. 2i, Supplementary Figs. 9i,j and 11f).”

Moreover, additional measurements using FT-STs on another CPHN **1** ribbon on Br/Ag(111) with a truncated right terminus (Supplementary Fig. 23a,b) give the consistent conclusion. The line-grid STS map (Supplementary Fig. 23c) does not show a zero-bias end-localized state at the truncated terminus. Although a constant-current dI/dV map at 0.03 V shows enhanced intensity near the right end (Supplementary Fig. 23j), the point spectra (Supplementary Fig. 23e) indicate that this signal corresponds to the spatial tail of a quantum-well state at ~ 0.03 eV, rather than a state pinned at E_F . We emphasize that the STS maps and FT-STs consistently show a similar metallic band crossing E_F , even though the termination of this CPHN **1** ribbon is different from that in Fig. 4c and Supplementary Fig. 24a.

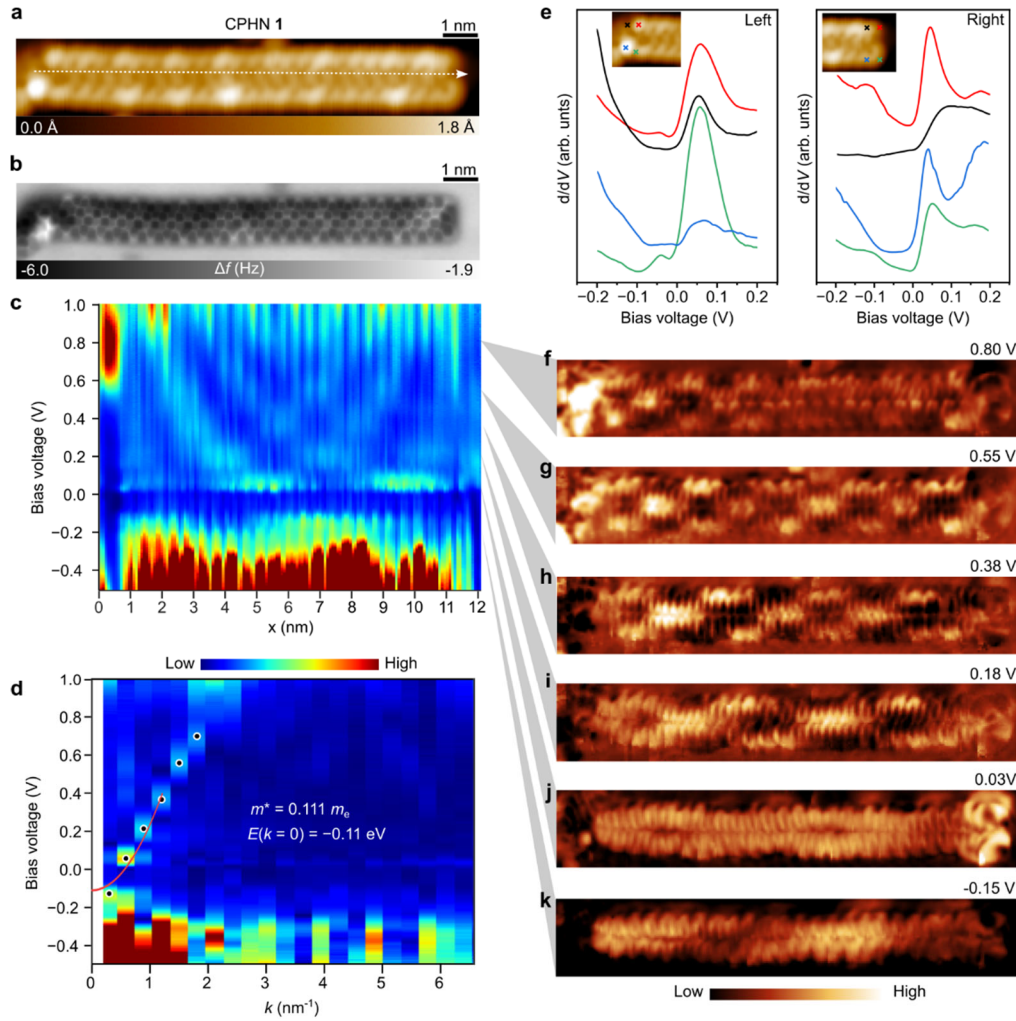
Taken together, these datasets show that the near- E_F spectral features evolve with ribbon length and local environment, as expected for finite-size quantized states and electrode-induced level alignment, rather than exhibiting a termination-protected, length-insensitive mid-gap end mode. As to the possible topological end mode, we have added several sentences in SI Section 8. It reads, “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 [Altland, A. & Zirnbauer, M. R. Nonstandard symmetry classes in mesoscopic normal-superconducting hybrid structures. *Phys. Rev. B* **55**, 1142-1161 (1997); Chiu, C.-K., Teo, J. C. Y., Schnyder, A. P. & Ryu, S. Classification of topological quantum matter with symmetries. *Rev. Mod. Phys.* **88**, 035005 (2016).]”



Supplementary Fig. 18 | DFT calculation of electron transmission and density of states in a two-electrode device.



Supplementary Fig. 11 | Transport and STS measurements on the same single-terminated CPHN 1 ribbon.



Supplementary Fig. 23 | QPI characterization of a CPHN 1 ribbon with a truncated terminus.

Beyond this conceptual discrepancy, there are further issues with the LDOS patterns and their Fourier transforms. The experimental QPI dataset is very limited: across the main text, Extended Data, and Supplementary Information, the LDOS patterns and FT-dI/dV line profiles appear to be essentially the same data as in Fig. 4e (CPHN1) and Fig. 4m (CPHN2), without additional independent measurements. The STM and AFM images of the ribbon segments used for the LDOS line profiles never show the actual termini of the ribbons, although these termini are crucial for the formation of standing waves. The data should cover the full ribbon length and clearly indicate the positions where dI/dV spectra were recorded. In addition, the parabolic fitting of the FT-LDOS patterns, for example in Supplementary Fig. 19, is performed only over the first few low-energy points. Either the fit should be carried out over the full accessible energy range, or the authors should justify why it is restricted to small energies. Finally, the agreement between experimental and computed LDOS maps in Fig. 4m,n is rather poor in terms of the positions of the intensity maxima, whereas the corresponding Fourier-transformed maps

in Fig. 4o,p look surprisingly similar. The authors should explain how good agreement is obtained in Fourier space despite visible discrepancies in real space.

Reply:

We thank the referee for these detailed comments. We agree that the QPI/LDOS presentation and analysis in the previous version were not sufficiently in detail, and we have addressed each point with new measurements, improved annotation, and revised modeling.

1. “Limited” QPI dataset/lack of independent measurements

We agree that the manuscript previously gave the impression that the FT-LDOS analysis relied on essentially a single representative dataset for each ribbon type. In the revised manuscript, we have therefore included additional independent QPI measurements on CPHN 1 and CPHN 2 defect-free segments with lengths comparable to those analyzed in Fig. 4. Two additional CPHN 1 datasets (Supplementary Figs. 23 and 24) reproducibly show clear finite-size QWS quantization, with discrete levels spanning across (E_F) and exhibiting level spacings comparable to those in Fig. 4, as expected for standing waves in finite 1D conductors. One additional CPHN 2 dataset (Supplementary Fig. 25) likewise reproduces a semiconducting dispersion with a band gap of ~ 0.18 eV, close to the 0.22 eV obtained in Fig. 4o.

Supplementary Figs. 23 and 24 provide further examples acquired under the same measurement conditions as in Fig. 4, where the QPI characterization focuses on a defect-free interior segment and the termini are outside the mapped area; nevertheless, the extracted dispersions closely match those shown in Fig. 4. In addition, we now have included a newly conducted dataset (Supplementary Fig. 23) in which the termini of the CPHN 1 ribbon are explicitly identified by STM and nc-AFM and are also visible in the (dI/dV) maps, as requested by the referee. Notably, this ribbon segment contains a free end, which is advantageous for transport-type measurements, and we therefore performed a more comprehensive characterization on the same ribbon segment (STM, nc-AFM, (dI/dV) mapping and QPI). The corresponding QPI analysis again yields a metallic band structure consistent with Fig. 4e. Taken together, these independent datasets indicate that the metallic dispersion of CPHN 1 is robust and only weakly affected by the detailed terminal configuration. Therefore, we have kept the original CPHN 1 dataset in Fig. 4 as the representative example, and have provided the newly measured, termini-resolved dataset as additional support in Supplementary Fig. 23 rather than replacing Fig. 4. The QPI results of these additional examples are also provided in 3D view in the revised Supplementary Fig. 22g–l.

2. Ribbon termini not shown/spectra positions not indicated

We agree that the ribbon termini are crucial for standing-wave formation and must be

clearly shown. In the previous version, the ends were not displayed mainly for practical reasons: (i) the terminal electronic features can be very strong and visually dominate the contrast in the same dynamic range used to highlight the interior standing-wave patterns; and (ii) in some cases the local topography at/near the ends (often affected by tethering or attachment to nearby structures) is unfavorable for acquiring high-quality nc-AFM contrast.

To address this properly, we have now provided a full-length STM dataset (Supplementary Fig. 23) that explicitly includes both termini and have marked the exact line/line-grid positions used for dI/dV acquisition directly in the corresponding overview image (we have also clarified this annotation in Fig. 4c, where the line-grid position is indicated). Notably, the STS maps and FT-STs consistently show a similar metallic band crossing E_F , despite the fact that the termination of the CPHN 1 ribbon in Supplementary Fig. 23 is different from that in Fig. 4c and Supplementary Fig. 24a.

3. Parabolic fitting in Supplementary Fig. 19 (revised 24) only at low energies

We agree that the fitting range requires justification. Our intention was not to suggest that the full band is perfectly parabolic, but to extract an effective curvature (effective mass) near the band extremum, where a quadratic expansion is justified. In general, the parabolic (effective-mass) approximation is a local approximation around a band extremum (e.g., near Γ), obtained from the second-order Taylor expansion of $E(k)$; away from the extremum, real bands are typically non-parabolic, and the curvature (and thus any “effective mass” extracted from it) becomes energy dependent.

Accordingly, we cannot meaningfully fit the entire accessible energy window with a single parabola because the dispersion departs from a free-electron-like quadratic form at larger k . In the revised SI, we have therefore (i) explicitly stated that the parabola fit is restricted to the low-energy region near Γ to extract the local curvature, and (ii) added a short discussion to the figure caption of the Supplementary Fig. 26:

“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.”

4. Poor real-space agreement in Fig. 4m,n but similar Fourier-space maps in Fig. 4o,p

We acknowledge that the main discrepancy between the experimental and simulated real-space line STS maps is the missing intensity maximum on the left-hand side of the previous simulation (Fig. 4n), which is clearly present in the experimental map (Fig. 4m). In the earlier simulation, we extracted the LDOS only along the single central row

of carbon atoms. This choice provides unrealistically high spatial selectivity compared with the experiment, where the measured dI/dV signal effectively averages over a finite lateral extent due to the tip shape and finite spatial resolution.

To make the comparison more faithful, we have re-evaluated the simulated real-space map by integrating the LDOS over a wider lateral window perpendicular to the ribbon axis (i.e., including multiple adjacent carbon rows rather than only the central line). With this experimentally more realistic spatial averaging, the previously missing maximum on the left side now appears, and the updated simulation is shown in the revised Fig. 4n below. The corresponding FT-STs map has been updated accordingly and remains very similar to the previous version.

This also helps rationalize why the Fourier-space agreement can be good even when real-space maxima are somewhat shifted: local changes in termination geometry (e.g., non-hard-wall ends connected to PPTL/defect/tethering structures) and associated phase shifts can modify the detailed real-space intensity distribution, whereas the Fourier-space signal is primarily governed by the dominant scattering wavevector $q(E) \approx 2k(E)$ along the ribbon axis and is therefore comparatively robust to such real-space phase/boundary-condition variations. This behavior is well documented in FT-STs/QPI analyses (see, e.g., L. Simon *et al.*, J. Phys. D: Appl. Phys. **44**, 464010 (2011)).

Overall, we have revised the manuscript to (i) expand the QPI dataset with independent measurements, (ii) show full ribbon lengths including termini with clear acquisition-position markers, (iii) justify the restricted parabolic fitting as a near- Γ effective-mass extraction, and (iv) improve the real-space vs. Fourier-space comparison by extracting the simulated LDOS over a wider lateral window (more consistent with the experimental spatial averaging) and updating the corresponding FT-STs accordingly.

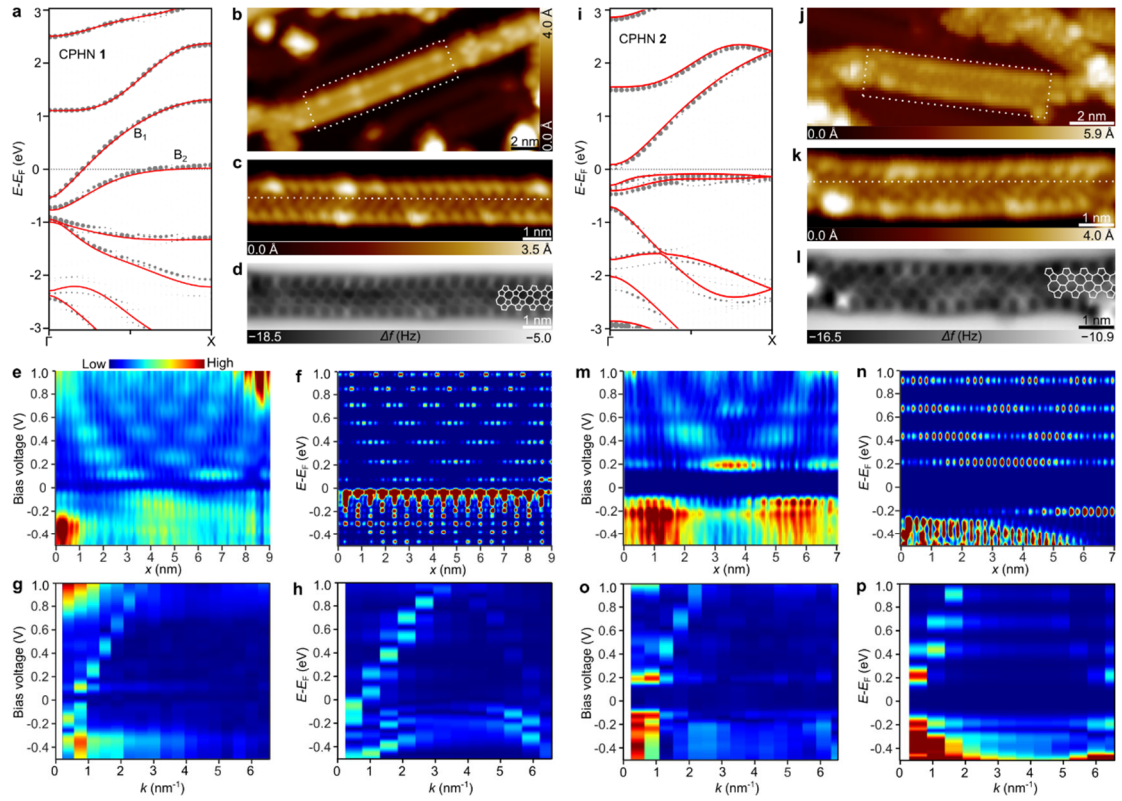
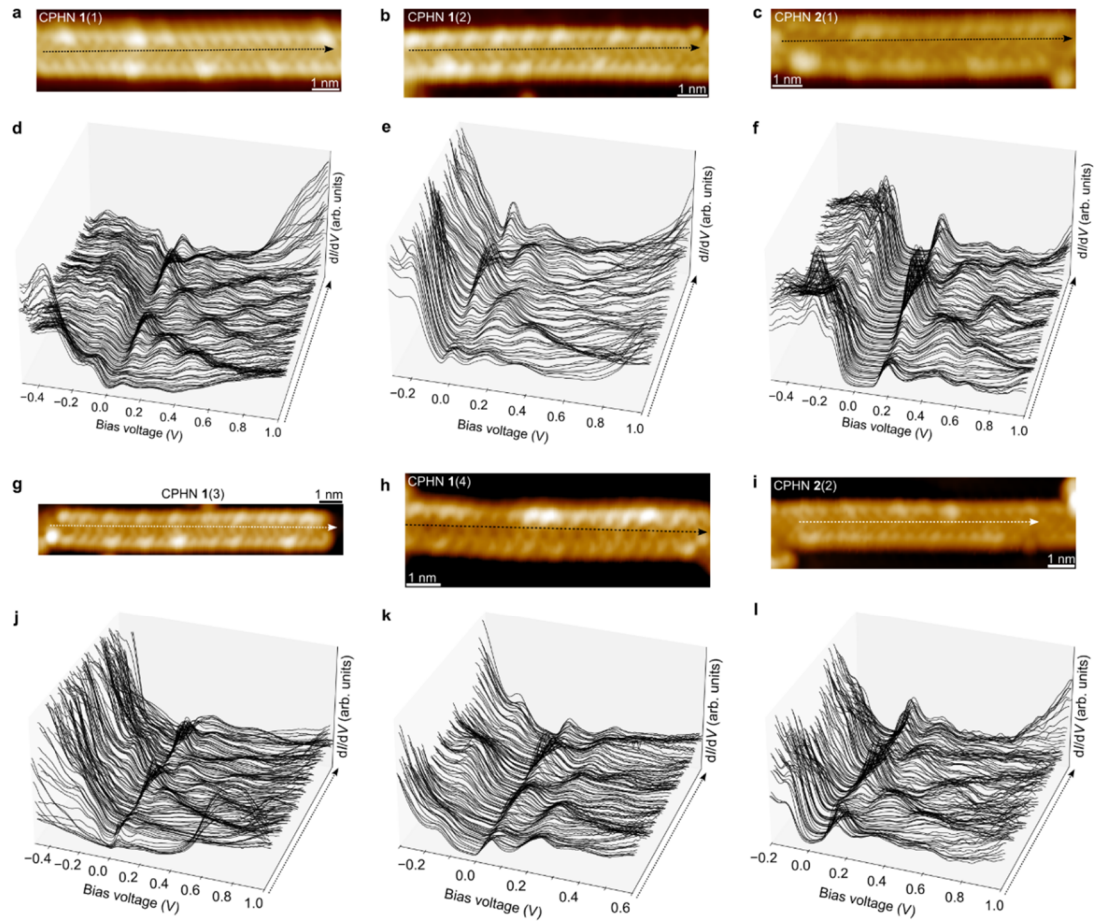
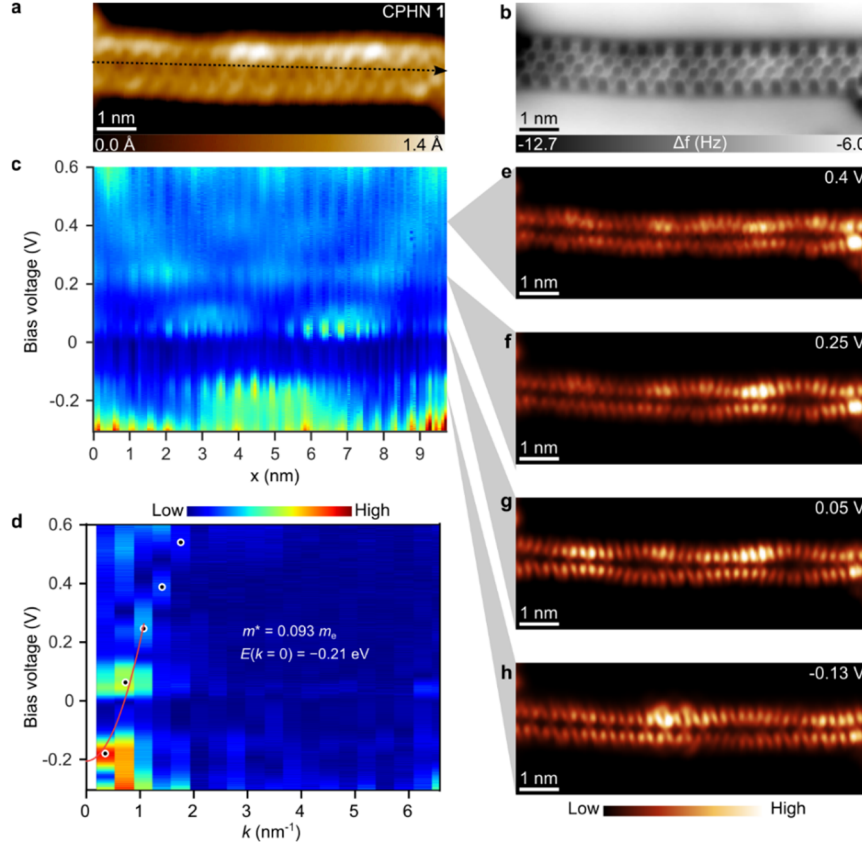


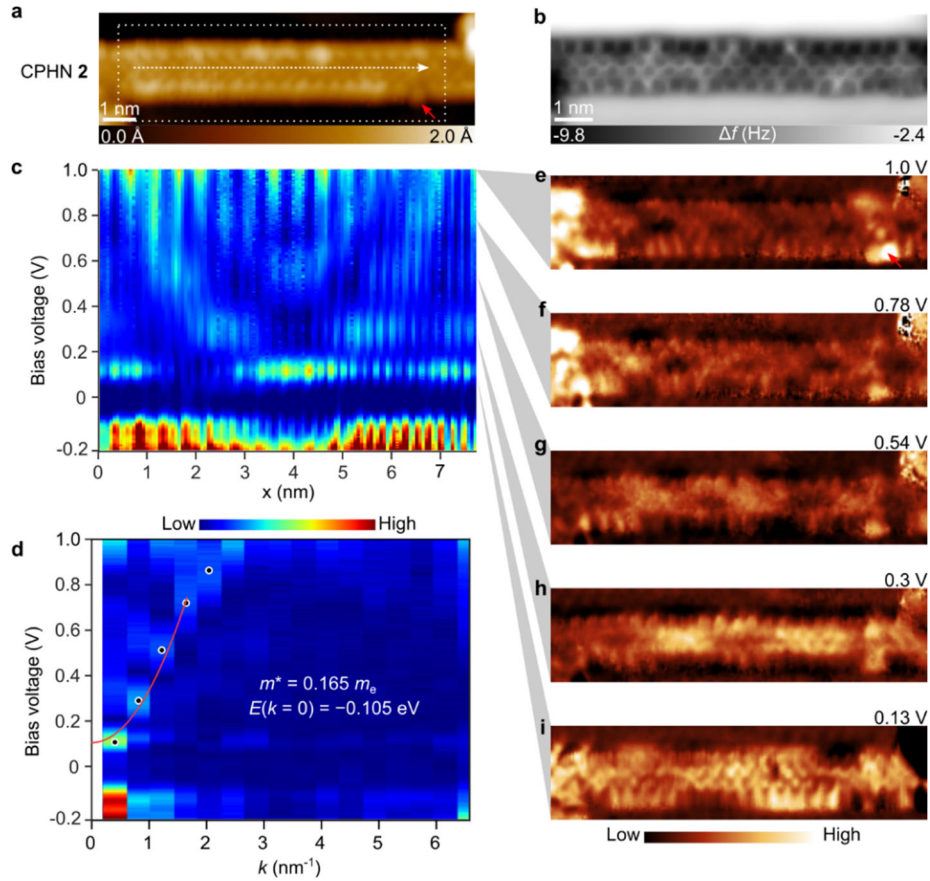
Fig. 4 | Electronic properties of CPHNs 1 and 2.



Supplementary Fig. 22 | 3D views of stacked dI/dV spectra of CPHNs.



Supplementary Fig. 24 | QPI characterization of an additional CPHN 1 ribbon.



Supplementary Fig. 25 | QPI characterization of an additional CPHN 2 ribbon.

4. It remains unclear how short, finite ribbons with discrete energy levels could support electron mobilities comparable to those of carbon nanotubes. The manuscript should address this point.

Reply:

We thank the referee for this comment. We believe the concern mainly reflects a terminology mismatch. In our manuscript we do not report or infer an electron mobility for CPHN **1** (which is typically a diffusive, device-extracted quantity). Instead, our comparison to metallic carbon nanotubes is made on the basis of the two-terminal contact conductance measured in the contact geometry.

Notably, the carbon-nanotube benchmark we cite [Science 280, 1744–1746 (1998)] is itself framed in exactly the same language: Frank *et al.* report that the conductance of arc-produced MWNTs is one unit of the conductance quantum G_0 and explicitly state that the nanotubes conduct current ballistically. They further explain that quantized conductance is expected when the conductor length is smaller than the electronic mean free path, in which case each conducting channel contributes G_0 . Experimentally, they observe a plateau at $1 G_0$ that remains constant over a micrometer-scale displacement and emphasize that this is consistent with a ballistic conductor and inconsistent with classical conductors where conductance scales inversely with length. Therefore, our statement “comparable to metallic carbon nanotubes” follows the same criterion used in Ref. 4: a quantum-limited conductance near G_0 as evidence of (near-)ballistic, single-channel transport, rather than any claim about mobility.

Regarding the referee’s point about finite ribbons with discrete levels: finite-size quantization in STS/QPI does not preclude a high contact conductance. In a contacted geometry, discrete QWS resonances are broadened by electrode coupling, and if one resonance is aligned (or pinned) near E_F , the low-bias transmission can approach unity, yielding $G \sim G_0$ for the dominant channel. Thus, the observation of a conductance close to G_0 in contact transport is fully consistent with a short 1D metallic conductor operating in the Landauer regime.

To eliminate any possible ambiguity that may have prompted the referee’s “mobility” wording, we have revised the manuscript text as detailed below:

1. **Original:** “..., ideally with a transport performance comparable to metallic carbon nanotubes.”

Revised: “..., ideally with a quantum-limited conductance comparable to metallic carbon nanotubes.”

2. **Original:** “The nearly ballistic transport behaviour of CPHN **1** is evidenced by its conductance close to the conductance quantum G_0 , comparable to that of metallic carbon nanotubes.”

Revised: “The CPHN **1** ribbon exhibits near-ballistic, near- G_0 quantum-limited

conductance, comparable to metallic carbon nanotubes.”

5. There is a typo in the caption of Extended Data Figure 6 (“Sin-unpolarized”).

Reply:

We thank the reviewer for pointing out this drawback, we have revised it accordingly.

6. The statement “The simulated results highly reproduce the experimental observations (Extended Data Fig. 8), providing further confirmation of the metallic and semiconducting nature of CPHN-1 and CPHN-2 in their finite lengths” is not scientifically rigorous. Whether a finite system exhibits metallic or insulating behavior depends on the Fermi-level alignment relative to the discrete quantized levels. Even an intrinsically metallic ribbon can appear insulating at finite length. If the authors intend to discuss the infinite-length limit, they should state this explicitly and revise the discussion accordingly.

Reply:

We thank the referee for pointing out that our previous statement was not sufficiently rigorous. We agree that for finite-length ribbon segments the LDOS at E_F is governed by discrete quantum well states (QWS) levels, and an intrinsically metallic ribbon may appear insulating if E_F falls between two quantized levels. Our intention was to use the simulations to support the underlying band character (metallic vs gapped) in the infinite-length limit, rather than to imply that every finite segment must be metallic/insulating independent of level alignment.

To address this, we have revised the manuscript text accordingly. The original sentence:

“The simulated results highly reproduce the experimental observations (Extended Data Fig. 8), providing further confirmation of the metallic and semiconducting nature of CPHN 1 and CPHN 2 in their finite lengths, respectively.”

has been replaced by:

“The simulations capture the observed quantum well states quantization and dispersive features in finite segments (Extended Data Fig. 8), consistent with a metallic band crossing for CPHN 1 and a gapped (semiconducting) band structure for CPHN 2 in the infinite-length limit.”

This revision explicitly separates the finite-size quantization observed experimentally from the metallic/semiconducting assignment in the thermodynamic limit, thereby resolving the referee’s concern.

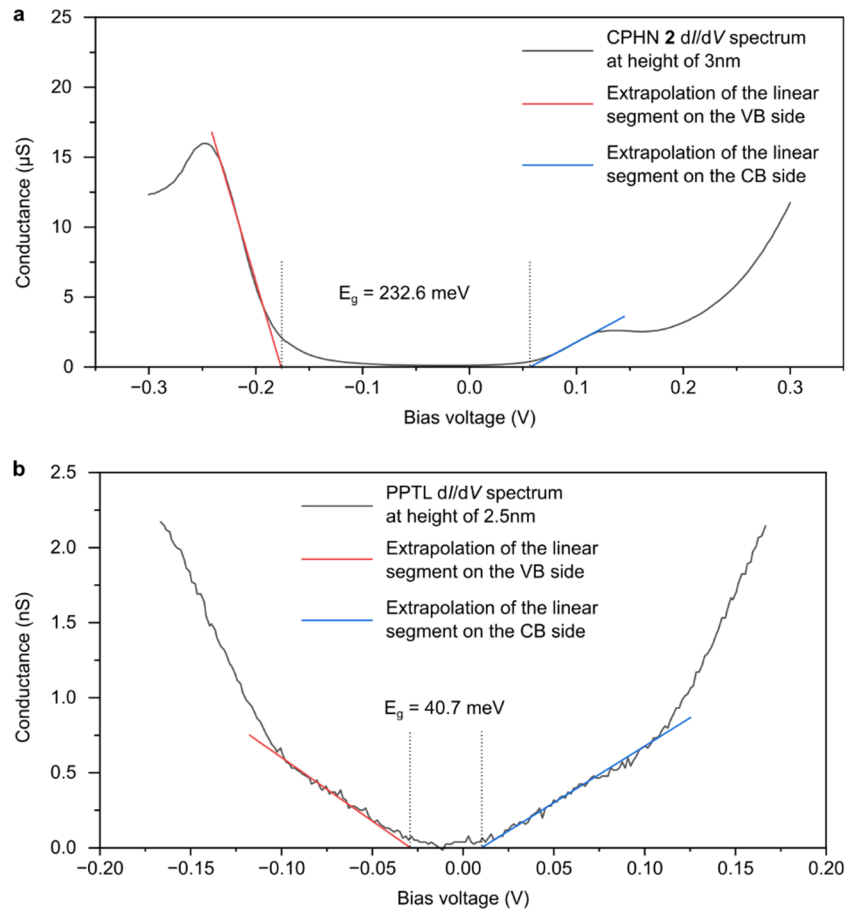
7. The criteria used to determine energy gaps from transport measurements are not clearly

defined. It is unclear how the values of 0.24 eV (CPHN2, ED-Fig. 4) and 50 meV (PPTL, Supplementary Fig. 10) are obtained. In addition, the reliability of transport measurements on very short nanoribbon segments—as shown in ED-Fig. 4b and Supplementary Figs. 9e and 9f—needs to be evaluated, since end states or defects may dominate the observed behaviour.

Reply:

We thank the referee for pointing out that the criteria used to extract energy gaps from the contact-transport $dI/dV(V)$ spectra were not sufficiently defined, and for raising the concern that transport on very short segments may be dominated by end states or defects.

(i) Definition of the transport gap. In the revised manuscript, we explicitly define the reported values as transport gaps extracted from the differential conductance as $E_g = e(V_+ - V_-)$, where V_- and V_+ are the onset biases on the occupied and unoccupied sides, respectively. We determine V_- and V_+ using a standard linear-extrapolation (line-intersection) procedure commonly used in STS to estimate band edges/band gaps [Commun. Mater. 4, 82 (2023); Phys. Rev. B 50, 4561–4570 (1994)], as illustrated in Supplementary Fig. 12. Specifically, we fit straight lines to the quasi-linear leading-edge segments of the first occupied-side (VB) and unoccupied-side (CB) rises closest to E_F . We then define V_- and V_+ as the intersection points of these leading-edge fits with the low-conductance background (baseline; black dashed line).



Supplementary Fig. 12 | Transport-gap extraction by linear extrapolation (line-intersection method).

(ii) **Reliability for short effective lengths/role of end states.** We address the referee's concern about possible end-state contributions by combining experiment and calculation, both of which consistently show that terminal states do not dominate the near- E_F features relevant for our transport-gap/onset analysis.

On the experimental side, end-site STS and real-space dI/dV maps do not reveal a robust, localized zero-energy end mode pinned at E_F . Instead, the spectral weight around E_F is broadly distributed along the ribbon, and the near-zero-bias enhancement observed in contact transport is accompanied by LDOS that remains substantial in the interior rather than being confined to the termini (Supplementary Figs. 11 and 23). Notably, the STS maps and FT-STs consistently show a similar metallic band crossing E_F even when the ribbon termination is changed (e.g., truncated versus defective junction), arguing against a termination-protected end state as the origin of the transport anomaly (Supplementary Fig. 23; compare with Fig. 4c and Supplementary Fig. 24a).

On the computational side, we analyzed the projected DOS of the contacted junction geometries (Supplementary Fig. 18g–i, Supplementary Section 9). The near E_F feature relevant for transport is not dominated by the terminal parts adsorbed on the Ag leads. Instead, the projected DOS shows a larger contribution from the central freestanding (bulk-like) segment than from the terminal/contact region (comparison between the Center and Lead projections). This indicates that the conductance onset and the enhanced transport around E_F are governed primarily by extended, bulk-like states of CPHN **1**, while terminal states provide only a secondary contribution. Therefore, even for these nanometer-scale junction lengths, the measured conductance remains a reliable probe of the intrinsic (bulk-like) metallic transport of CPHN **1** rather than being an artifact of end-localized modes.

8. In the tight-binding model, the positions and physical meaning of the a, b, and c sites within a single unit cell are not clearly described. Showing the corresponding atomic orbitals would significantly improve the clarity of the model.

Reply:

We thank the reviewer for pointing out that the definition and physical meaning of the a, b, and c sites in the tight-binding model were not sufficiently clear. In our model, the a/b/c sites do not correspond to individual carbon atoms. Instead, we adopt an effective π -only description in which each pentalene unit is represented by three localized Wannier-center-based basis sites

(labeled a, b, and c) constructed from the underlying carbon $2p_z$ manifold.

To improve clarity, we have now explicitly clarified the basis definition in the Methods and added a schematic visualization of the real-space centers of these basis states in Supplementary Figs. 15d, 16a, and 17a, thereby making the positions of the a/b/c sites within a unit cell unambiguous. We have also revised the tight-binding description to state clearly that the PPTL Hamiltonian is defined on a three-orbital-per-unit-cell basis including nearest-neighbor (NN) and next-nearest-neighbor (NNN) hopping terms. For CPHN **1** and **2**, we have further clarified that the coupled system is described using a six-orbital basis per unit cell $\{a, b, c, a', b', c'\}$, corresponding to two coupled PPTL chains.

In addition, to address the reviewer’s request for a clearer description of the basis construction and parameter determination, including why the effective centers differ between PPTL, CPHN **1**, and CPHN **2**, we have added a new paragraph in **Supplementary Section 8**, reproduced below for completeness:

“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 pentalene repeat unit, motivating a minimal three-site SSH description. Accordingly, we define three effective lattice sites (Wannier centers) per pentalene 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 believe these revisions substantially improve the transparency of the tight-binding model and the correspondence between the effective basis sites and the underlying π -electron framework.

The revised Methods now read: “We construct an effective π -only tight-binding model for PPTL by using three localized Wannier-like π orbitals per pentalene unit as the basis states, labeled $\{a, b, c\}$. The real-space centers of these Wannier-like orbitals are illustrated in Supplementary Figs. 15d, 16a, and 17a. ...; ...For CPHN **1** and **2**, we use a six-orbital basis per unit cell, $\{a, b, c, a', b', c'\}$, which represents two coupled PPTL chains ”

Regarding the authors' reply and other reviewers' comments

9. All three reviewers noted that the TERS data do not align with the calculations. The authors attribute this discrepancy to surface adsorption, but the strong structural disorder and frequent joint fusions likely play a more significant role. The authors should examine the reproducibility of the Raman spectra to rule out large variations caused by structural defects, which may also affect the electronic properties.

Reply:

We thank the referee for the comment and for highlighting the potential impact of structural imperfections on spectroscopy. We would like to clarify that our decision to remove the TERS data in the revised manuscript is not driven by an attempt to “avoid” an imperfect agreement, nor does it imply that our STM/STS/QPI/transport conclusions are dominated by uncontrolled defects.

As we already noted in our first-round rebuttal, the remaining mismatch between the measured TERS spectra and the calculations cannot be attributed solely to the adsorption geometry of CPHNs. A major methodological factor in TERS is the tip–substrate plasmonic nanocavity, whose near-field distribution (polarization, confinement volume, and field gradients) depends sensitively on the actual tip apex geometry and tip–sample configuration. This can alter Raman selection rules and strongly reweight vibrational modes (often enhancing modes with out-of-plane or near-field–coupled components), such that the experimental spectra are not expected to match conventional Raman calculations that assume idealized excitation/collection conditions. Achieving a quantitative comparison would require an explicit electrodynamic treatment of the realistic tip apex and nanocavity field, coupled to mode-resolved Raman/TERS

simulations—an analysis that is technically detailed and beyond the scope of the present work. We view this as an important topic on its own and plan to address it in a dedicated study.

Importantly, our TERS spectra were acquired on the central regions of the ribbons, away from the termini where tethering and joint fusions occur most frequently, so the specific end-connected motifs mentioned by the referee are unlikely to dominate the measured TERS response in the first place. Nonetheless, because TERS is not essential for the structural assignment or the electronic conclusions in this manuscript, we chose the most conservative approach and removed the TERS dataset and its interpretation, so that the main claims rely exclusively on STM/nc-AFM structural identification and on STS/QPI/contact-transport data.

Finally, we emphasize that the potential influence of terminal defects is already controlled in our electronic measurements by design: STS/QPI analyses are performed on well-defined ribbon segments (with acquisition positions indicated and away from ambiguous junction regions), and our conclusions are based on reproducible features such as finite-size QWS quantization and dispersive behavior. The removal of TERS therefore reflects the complexity of quantitatively modeling the plasmonic nanocavity in TERS—not a general sensitivity of all our spectroscopies to defects.

10. As noted by Reviewer 2, the yields of CPHNs remain low. The authors claim improved yield, but the supporting statistical analysis is still insufficient. The sample quality shown in the revised submission remains poor.

Reply:

We thank the referee for reiterating the concern regarding yield and sample quality. We agree that the overall yield of CPHNs is not as high as in some benchmark on-surface nanoribbon syntheses (e.g., stepwise Ullmann coupling followed by cyclodehydrogenation). In the revised manuscript we have therefore taken care to (i) present the yield evaluation procedure more transparently and conservatively, and (ii) avoid overstating “improved yield” beyond what is directly supported by the statistics.

At the same time, we would like to emphasize that the level of terminal tethering, bending, and junction formation visible at high coverage is a common outcome in high-temperature on-surface synthesis of extended nanoribbons, and similar sample morphologies are frequently encountered in other high-impact reports of exotic GNRs (including ZGNRs and Janus GNRs). In this context, the key practical metric for many electronic measurements is not the global areal yield or the visual impression of a crowded network, but the availability of sufficiently long, well-defined ribbon segments for characterization. In our samples we reproducibly obtain defect-free CPHN segments on the order of ~10–20 nm, which is comparable to, and in many cases exceeds, what is shown for several previously reported exotic nanoribbon systems.

Most importantly, the central conclusions of our work do not rely on a claim of high synthetic yield. Our identification of the metallic nature of CPHN **1** is based on the underlying band character (in the infinite-length limit) supported by STS/QPI and theory, and on the consistently high contact conductance close to G_0 , demonstrating near-quantum-limited transport. These conclusions are extracted from well-defined individual ribbon segments and remain robust irrespective of the overall sample coverage or the presence of tethered junction regions elsewhere on the surface. We therefore believe that, while further yield improvements are certainly desirable for future device-oriented studies, the current sample quality is sufficient to establish CPHN **1** as a conductive, carbon-based prototype quantum wire with near- G_0 transport characteristics.

11. The authors' reply regarding the zero-bias peak in CPHN1 is not convincing. The peak appears consistently across all transport measurements, which contradicts the claim that it arises only when the metallic band minimum accidentally aligns with the Fermi level. Presenting conductance over a larger bias range would help determine whether quantum well states are present and clarify the origin of the zero-bias anomaly.

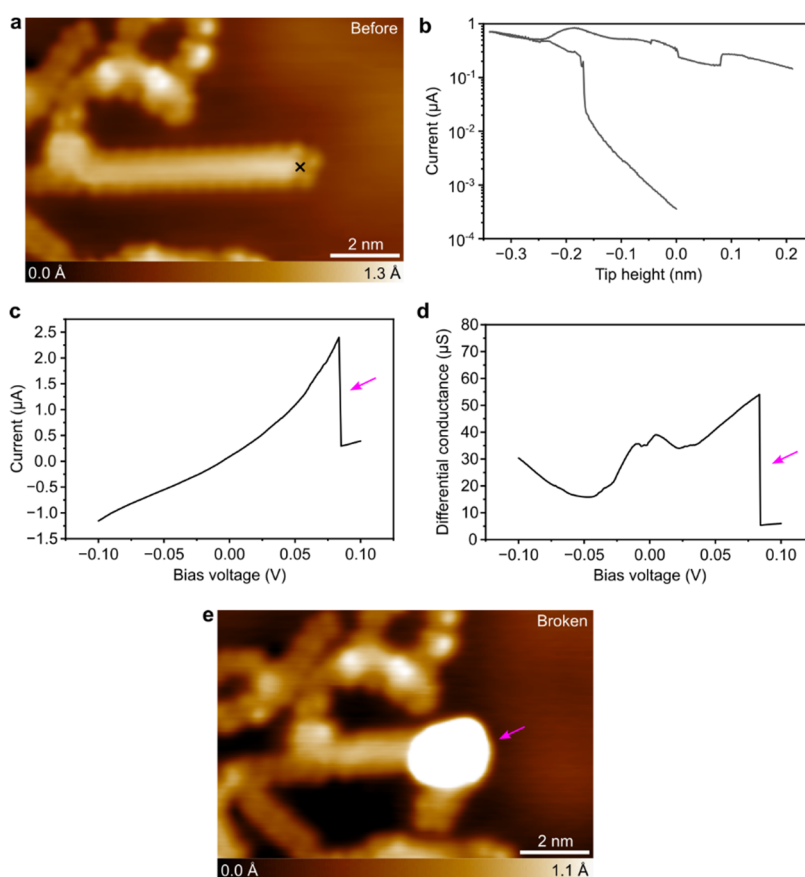
Reply:

We thank the referee for the further comment on the origin of the zero-bias peak in the contact-transport of CPHN **1**. We agree that an explanation based on an “accidental” alignment of a finite-size level with E_F would be inconsistent with the observation that the zero-bias feature appears reproducibly across all measured junctions. We therefore clarify that our interpretation is not accidental alignment, but Fermi-level pinning under contact conditions: in the lifting/contact geometry, charge transfer and electrostatic equilibration with the metallic tip/electrode can drive one discrete resonance (QWS) toward E_F and pin it there, yielding a robust zero-bias anomaly. This is also discussed in reply to comment #3 above.

Regarding the referee's request to present conductance over a substantially larger bias range, we agree that such data would, in principle, be valuable to directly visualize additional QWS resonances at higher energies. However, for CPHN **1** this is technically constrained by the intrinsically high conductance of the contacted ribbon in our STM lifting junctions. In our measurements, the current already exceeds 10 μA at biases of ± 0.2 V. This is close to the practical operating limit of our STM-based transport setup: conventional STM feedback and imaging are typically performed with transimpedance amplifier settings optimized for the nA regime (e.g., $\leq 10\text{nA}$), whereas operation in the μA regime requires a much lower gain with substantially reduced current sensitivity. Although we used the 10 μA range to enable the transport measurements, this setting already makes stable feedback control and simultaneous high-quality STM imaging challenging due to limited current resolution.

As a result, extending the bias range substantially beyond ± 0.2 V for CPHN **1** is not feasible

within the intrinsic constraints of STM lifting transport, precisely because the junction conductance is so high. This situation differs from lower-conductance systems, such as semiconducting graphene nanoribbons (e.g., 7-AGNR), where wider-bias sweeps can be performed without driving the current into the μA regime. In addition, the combination of large current and high bias leads to significantly increased Joule heating in the contacted CPHN **1** junction, which can irreversibly damage the ribbon. We have illustrated this limitation by the example shown in Supplementary Fig. 13, where a I - V sweep with current up to $2.5\ \mu\text{A}$ already destroys the CPHN **1** ribbon. However, within the accessible bias window, the reproducible zero-bias feature together with the additional contact-geometry calculations supports Fermi-level pinning as the most consistent explanation.



Supplementary Fig. 13 | Irreversible damage of a CPHN **1 ribbon during an I - V sweep in the transport experiment.**

In conclusion, the study addresses an interesting novel type of nanoribbon, but in my view the current version does not yet provide the structural control, data completeness, and electronic characterization required to support the central claims. I would encourage the authors to revisit these points comprehensively.

Reply:

We thank the referee for the overall assessment and for acknowledging that our work introduces an interesting and novel type of nanoribbon system. We fully agree that structural control and data presentation are critical for supporting the central claims, and we have therefore made substantial efforts in the revision to address the referee's concerns comprehensively: we have expanded the high-resolution STM/nc-AFM dataset and clarified the statistical treatment of yield; we have improved the transparency and completeness of the QPI/LDOS analysis by adding independent measurements, showing full ribbon lengths with acquisition positions marked, and refining the fitting and simulation rationale; and we have clarified the interpretation of the electronic characterization by explicitly distinguishing finite-size quantization from the infinite-length band character and by providing additional calculations to rationalize the robust zero-bias feature in contact transport.

We hope these additions and clarifications resolve the remaining ambiguities. Importantly, while the overall synthetic yield can certainly be further improved in future work, the revised dataset demonstrates that well-defined CPHN segments are reproducibly accessible and that their key electronic signatures, metallic band character for CPHN 1 and near-quantum-limited conductance in contact transport, are robust. We therefore believe the revised manuscript now provides a complete and internally consistent foundation for the central conclusions.

Referee #3 (Remarks to the Author):

This is the review for the revised version of the manuscript (MS) "Realising narrow carbon pentaheptite nanoribbons with strong metallicity" by Huang et al.

All my comments have been replied to in satisfactory manner. The authors have included additional experimental and theoretical data which significantly improved the MS and made it more convincing. In my opinion, also the issues raised by the other reviewers have been addressed well (there were several similar/closely related comments between reviewers).

I have only two final minor comments (see below) and recommend publication of the MS in Nature.

Minor comments:

#1: In their reply to my comment #6, the authors write that the conductance peak around zero bias should not be assigned to a vHS. But in the revised version of the MS, they write on p. 12, l. 18f, that "The high DOS near the E_F can be attributed to contributions from the van Hove singularity (VHS) states of band B-2 [...]" Either I am misunderstanding this sentence or it contradicts the authors' statement from their reply. Please comment/correct/reformulate.

Reply:

We thank the referee for pointing out this potential inconsistency. We agree that our wording was not sufficiently precise and may be read as contradictory. The resolution is that the near-zero-bias features in tunnelling STS and in contact transport have different physical origins, and that the roles of band B_1 and band B_2 are distinct.

1. Tunnelling STS/QPI on finite segments (origin of the zero-bias peak).

In finite-length CPHN **1** segments, the occasionally observed peak at (or very close to) zero bias in STS arises from the alignment of a discrete QWS level derived from band B_1 with E_F for a given segment length and local electrostatic environment. In this finite-size regime, it is therefore not appropriate to assign the STS zero-bias peak to a van Hove singularity (VHS), which is defined for the infinite-length band structure.

2. Contact transport dI/dV : broad near-zero enhancement vs robust zero-bias anomaly.

We have added a paragraph to address the origin of zero-bias anomaly on the basis of our transport calculations, it reads “Our transport calculations for CPHN **1** adsorbed on two Ag electrodes (Supplementary Fig. 18 and Supplementary Section 9) reveal a zero-bias transmission state arising from Fermi-level pinning [You, S. *et al.* Quantifying the conductivity of a single polyene chain by lifting with an STM tip. *Nat. Commun.* **15**, 6475 (2024).] of a quantum well state (QWS) derived from metallic band B_1 , whose wavefunction spreads over the CPHN **1**. The electron transfer from the electrodes to CPHN **1**, as observed for CPHN **1** on bare Ag in Extended Data Fig. 6b, may facilitate the Fermi-level pinning. This Fermi-level pinning can explain the zero-bias differential conductance peaks observed experimentally in various CPHN **1** samples (Fig. 2i, Supplementary Figs. 9i,j and 11f).”

Importantly, this B_2 -related DOS enhancement should be distinguished from the robust zero-bias anomaly that appears consistently across transport junctions. Motivated by the referee’s and other reviewers’ comments, we performed additional contact-geometry calculations, which show that the universally observed zero-bias anomaly is best explained by Fermi-level pinning of a B_1 -derived QWS resonance to E_F under contact/lifting conditions, yielding a persistently high transmission at zero bias. In this interpretation, B_2 (including its VHS) contributes to the near- E_F background/broad enhancement, whereas the robust near zero-bias peak itself is governed by contact-induced pinning of a B_1 -QWS. The inappropriate description has been deleted in the revised manuscript.

#2: In Extended Data Fig.9 i,j the labels on the y axis read "Bias voltage (V)". Should this maybe be " $E-E_F$ (eV)", as in panels f and g?

Reply:

We thank the reviewer for careful reading of our work, the figure has been revised accordingly.

Referee #4 (Remarks to the Author):

I co-reviewed this manuscript with one of the reviewers who provided the listed reports.

This email has been sent through the Springer Nature Manuscript Tracking System NY-610A-SN&MTS

Reply:

We thank the reviewer for his valuable assessment of our work.

Referees' comments:

Referee #2 (Remarks to the Author):

General assessment

I appreciate the effort the authors have made to revise the manuscript and to address several of the previously raised points. However, after carefully examining both the revised version and the rebuttal, I remain unconvinced that the central claims are sufficiently supported. My concerns relate to the structural quality and yield of the material, the rigor and internal consistency of the electronic data interpretation, and the actual level of advance relative to prior work.

A recurring issue throughout the manuscript is that the interpretation appears to be guided by the intended conclusion, namely the claim of intrinsic metallicity, rather than being strictly derived from the experimental observations. Several key arguments rely on selective interpretation of the data, while alternative explanations are not rigorously considered or excluded. In its present form, the work is interesting and may be suitable for a more specialized journal, but it does not reach the level of clarity, rigor, and unambiguous evidence expected for publication in Nature.

Response: We thank the referee for the careful reassessment. To address the three main concerns, we have revised the manuscript accordingly: (1) We now explicitly acknowledge the current yield limitations and clarify that structural assignments are restricted to identifiable CPHN segments, avoiding any implication of device-ready macroscopic synthesis. (2) We distinguish finite-size quantization, contact-induced effects, and the intrinsic long-ribbon band character; our claim of intrinsic metallicity for CPHN **1** is now grounded strictly in DFT/TB and FT-LDOS/QPI dispersion crossing E_F , while the transport data are moderated as a possible contact-induced resonance. (3) We better contextualize the advance by differentiating our non-benzenoid pentaheptite backbone from prior zero-mode-superlattice strategies, and highlight our combined FT-LDOS and transport evidence. We have toned down application-oriented claims, presenting CPHN **1** as a prototype platform rather than a device-ready material.

Structural quality and statistical analysis

The most serious concern is the discrepancy between the structural quality evident in the STM images and the reported statistical yield. The statistical analysis remains unconvincing. Many segments classified as target CPHN ribbons are clearly defective, bent, or involved in junctions, and therefore cannot reasonably be considered well-defined nanoribbons. This becomes particularly evident when inspecting the marked “target ribbons” (yellow segments), where a

significant fraction is structurally imperfect, short, or part of fused networks. In the attached PNG, I have indicated several such examples (red circles) where the assignment appears questionable.

The counting procedure, based on pentalene units and area normalization, does not reflect the actual usability of the structures for electronic characterization and effectively inflates the yield by including structurally ambiguous or defective motifs. A truly defect-free segment should be straight, isolated, and sufficiently long, on the order of at least ten repeat units, yet such segments appear to be rare in each presented scan frame. Consequently, the reported yield does not correspond to the yield of physically meaningful nanoribbons, which undermines both the statistical analysis and the reliability of the subsequent electronic measurements.

Response: We thank the referee for this critical distinction. We agree that structural assignability does not equal suitability for electronic characterization. We have therefore re-analysed the statistics by excluding structurally ambiguous segments. The revised total CPHN yield is 16.7%. More importantly, well-defined segments containing at least six repeat units (>3 nm)—which are sufficient for our STM/QPI and transport measurements—account for $\sim 13.5\%$ under optimized conditions. Accordingly, we have updated the main text (total yield from 17.7% to 16.7%, added the 13.5% long-segment figure, and removed absolute individual yields) and revised Supplementary Fig. 4.

We have revised the manuscript and Supplementary Information accordingly. In the main text, we changed the CPHN 1/2 yield from 17.7% to 16.7%, removed the previous absolute yields for CPHN 1 and CPHN 2 while retaining their ratio of approximately 1:0.9, and added the following sentence: “*Although the global yield remains limited, well-defined CPHN segments containing at least six repeating units are reproducibly obtained with a yield of $\sim 13.5\%$, sufficient for the local measurements below.*” In the Supplementary Information, we updated Supplementary Fig. 4b,f–h with the revised counting data and annotations, and revised the corresponding yield values in the Supplementary Fig. 4 caption.

Relation to prior work

The conceptual advance relative to prior work is not convincingly established. Carbon chains containing 5/7-membered carbon rings have already been reported in earlier studies (JACS 2019, 141, 44, 17713–17720; JACS 2020, 142, 23, 10291–10296), where the concept of lateral fusion employed in the present manuscript is essentially the same as that introduced in the 2019 work. Importantly, the principal limitation of this approach, namely the low yield of the target structures, remains unresolved here.

With respect to electronic properties, the manuscript does not convincingly establish a

substantive advance beyond the metallic graphene nanoribbons reported in *Science* 369, 1597–1603 (2020). In fact, the present system appears significantly more difficult to control, while not providing a clearly superior or fundamentally new electronic functionality.

Response: We thank the referee for the comparison. We agree that lateral fusion and 5/7 rings were reported previously. However, our key advance is the *fully* non-hexagonal (exclusive 5/7) backbone, enabled by an 8→5,5 rearrangement—which differs from prior mixed 5/6/7 systems. Yield remains limited, but we now state this explicitly and note that the resulting segments are sufficiently long for our QPI and transport measurements. Regarding the *Science* 2020 work, we have revised the text to distinguish our allotropic route (intrinsic 5/7 metallicity) from the zero-mode-superlattice approach in benzenoid GNRs; our combined QPI and transport evidence supports this distinct behavior. We have updated the Abstract and main text to acknowledge these prior works upfront and to moderate application-oriented claims.

In the Abstract, we have made a revision: “*Metallic graphene nanoribbons have been realized by band engineering, notably through zero-mode superlattices; however, atomically precise metallic nanoribbons of fully non-benzenoid carbon allotropes, such as the theorized metallic carbon pentaheptites, remain unexplored.*” We have also moderated the application-oriented wording to: “*This highlights CPHN 1 as a promising planar carbon metal and suggests a possible route toward carbon quantum wires, although further synthetic optimization will be required for device integration.*” In the beginning of the main text, we have added: “*In contrast to zero-mode-superlattice metallic GNRs, carbon pentaheptite offers an allotropic route to inherent metallicity based solely on fused five- and seven-membered rings.*”

Electronic structure and dispersion analysis

The analysis of the electronic structure raises several concerns. The extraction of a parabolic dispersion and the associated fitting appear misleading. Based on the presented data, the dispersion seems to originate from the Fermi level rather than from approximately -0.15 eV as drawn in the manuscript, and the fitting is restricted to a limited energy range without clear justification. This weakens the reliability of the extracted band parameters. A particularly striking example is SI Fig. 24d, where a parabola is fitted to three (3) data points. This does not make sense.

More generally, the manuscript does not treat the distinction between finite-size quantization and intrinsic metallicity in a sufficiently rigorous manner. The experimental data clearly show discrete quantum well states and energy gaps that depend on ribbon length and local environment. In addition, all spatially resolved STS maps for CPHN1 show a relatively homogeneous gap-like feature around the Fermi level, which appears fundamentally different from the higher-energy quantized gaps. No explanation is provided for this observation, and it

is not clear how this behavior is consistent with a simple metallic band crossing the Fermi level.

Response: We thank the referee for the detailed critique. We fully agree that the parabolic fits—especially those based on very few low- k points—should not be overinterpreted. We now explicitly state that these fits serve only as approximate guides for local curvature and are not central to our conclusions. The qualitative assignment of metallicity rests instead on the directly observed real-space QWS sequence: for CPHN 1, the first-envelope B_1 QWS appears below E_F ; for CPHN 2, it remains above E_F . We have also clarified that “intrinsic metallicity” refers to the long-ribbon band character, not to the absence of finite-size QWS spacings in finite segments. Regarding the near- E_F gap-like suppression, we now explain that it reflects addition-energy and local electrostatic (e.g., Coulomb) effects in finite junctions, rather than a true single-particle band gap—consistent with the FT-LDOS evidence that the QWS manifold crosses E_F . These clarifications have been added to the main text and Supplementary Information, and we have de-emphasized all fitted parameter values.

We have revised the manuscript and Supplementary Information to clarify the distinction between finite-size quantization and intrinsic metallicity by adding the statement in the main text: *“Thus, the discrete level spacings observed in finite CPHN 1 segments reflect quantum confinement and local boundary conditions, rather than a true band gap in the long-ribbon limit.”*

We also added a corresponding clarification in Supplementary Section 13: *“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.”*

In the caption of Supplementary Fig. 27, we added: *“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.”*

In Supplementary Section 13, we have added a conservative discussion of the near- E_F gap-like suppression in finite CPHN 1 segments, noting that electron addition/removal processes can be influenced by addition-energy and local electrostatic effects, including possible Coulomb-charging contributions, as known for supported metallic nano-objects in STM junctions. We also added Hong et al., Front. Phys. 1, 13 (2013) as a new Supplementary Reference 12.

Zero-bias peak and Fermi-level pinning

The explanation of the robust zero-bias peak in transport measurements remains unconvincing. I initially considered whether this feature could originate from Fermi-level pinning, as suggested by the authors. However, based on the calculations shown in Supplementary Fig. 18, there is no clear evidence supporting such an interpretation. The quantum well states appear to shift systematically with increasing ribbon length rather than exhibiting a distinct state pinned at the Fermi level.

Given that the zero-bias peak is observed consistently across different junctions, an explanation based on Fermi-level pinning requires stronger and more direct support than currently provided.

Response: We thank the referee for the scrutiny. We agree that our previous wording on Fermi-level pinning was too strong. We have thus revised the interpretation to a "possible contact-induced near- E_F level alignment" of a B_1 -derived QWS resonance. To test this, we have performed additional transport calculations with varying electrode overlap (new Supplementary Fig. 19), which show a B_1 -derived resonance near E_F —though not strictly pinned—supporting that charge transfer/hybridization can shift a QWS into the near- E_F region. We now explicitly state this as a plausible scenario, not definitive proof. Crucially, our central metallicity claim rests on the FT-LDOS/QPI evidence that the B_1 manifold spans E_F , not on this transport interpretation. We have replaced the strong claim in the main text with a conservative statement presenting the contact-induced alignment as a plausible explanation for the broad conductance enhancement.

We have replaced the previous strong statement in the main text with the following more conservative wording: *“Our transport calculations for CPHN 1 adsorbed on two Ag electrodes (Supplementary Figs. 18, 19 and Supplementary Section 9) reveal a near- E_F transmission resonance arising from a B_1 -band quantum well state (QWS), whose wavefunction is spatially extended over the CPHN 1 backbone. The charge transfer and hybridization between the electrodes and CPHN 1 (Extended Data Fig. 6b) can shift and broaden the QWS-derived resonances, providing a plausible contact-induced level-alignment scenario³⁰ for the broad near- E_F conductance enhancement observed experimentally in various CPHN 1 samples (Fig. 2i, Supplementary Figs. 9i,j and 11f).”*

Unresolved spectral features

Another unresolved issue is the presence of a gap-like feature near the Fermi level in several datasets, including Fig. 4e, Supplementary Fig. 23c, and Supplementary Fig. 24c. This feature is clearly distinct from the larger quantized gaps observed at higher energies and appears consistently across different measurements. Its origin is not explained and appears incompatible with the interpretation of a simple metallic band.

In addition, the spectra shown in Supplementary Fig. 23e exhibit pronounced asymmetric, Fano-like line shapes together with position-dependent broadening. Similar broadening behavior is also observed in the contact transport data (Supplementary Fig. 9i and j). It is

unclear how these features should be understood. In particular, it would be important to clarify whether such asymmetric line shapes are also present in background spectra and whether they reflect intrinsic properties or measurement-related effects.

Response: We thank the referee for this careful observation. The near- E_F gap-like suppression (Fig. 4e, revised Supplementary Figs. 24c, 25c) arises from finite-size/local-environment effects (e.g., Coulomb charging/addition energy) in finite segments, not from an intrinsic band gap; this is fully consistent with our FT-LDOS/QPI evidence showing that the QWS manifold crosses E_F in the long-ribbon limit (Supplementary Fig. 28b-e).

We apologize that the plot in previous version of Supplementary Fig. 23e have led to misinterpretation of our observations (it is now in revised version of Supplementary Fig. 24e). We have added a panel (Supplementary Fig. 24l) for a direct comparison by plotting the spectra from the ribbon interior with the spectra at the right and left terminals in an added panel. As shown in Supplementary Fig. 24l, 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, but not from “asymmetric Fano-like lineshapes”. The interior spectra data set in Supplementary Fig. 24l is replotted from the spectra in Supplementary Fig. 23j of the CPHN **1** (Supplementary Fig. 23g), from the same CPHN **1** segment as in Supplementary Fig. 24a,e. The revised Supplementary Fig. 24 is duplicated below.

To further examine whether these terminal features could originate from independent end-localized states accidentally at zero bias, we additionally analyzed the state-resolved LDOS/charge-density distributions of the finite CPHN **1** model used in Extended Data Fig. 8a–c. As shown in Fig. R1, the enhanced intensity near the right terminus appears as part of the spatial distribution of each QWS orbital itself; no separate terminal-localized state distinct from the QWS manifold is observed. This calculation supports the experimental conclusion that the enhanced terminal DOS mainly reflects the tails and spatial-envelope asymmetry of extended QWS signals, rather than a Fano-like zero-bias mode.

The observed near- E_F QWS-dependent spectral features on the positive-bias side of the terminals on Br/Ag(111) (Supplementary Fig. 24l) 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 “asymmetric Fano-like line shapes” of zero-bias mode.

Regarding to the broadening peak around the E_F in the contact transport data, we are now more confident that the behavior can be reasonably assigned to the near- E_F transmission resonance arising from a B_1 -band quantum well state (QWS), reasonably attributed to a contact-

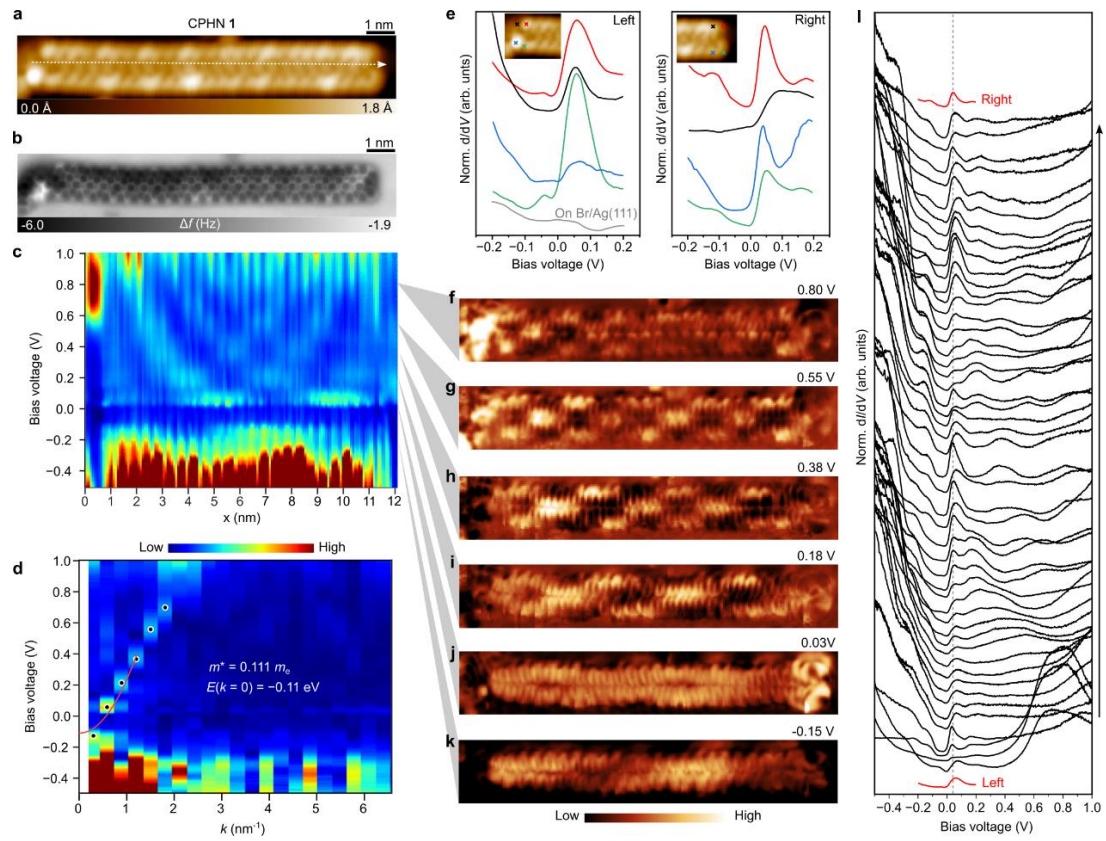
induced level-alignment scenario, which have been addressed in the revised descriptions in the main text, and supported by the additional transport calculations (Supplementary Figs. 18, 19).

The background spectra (correspondingly taken at the Ag(111) or Br/Ag(111) substrate), the missing information in our previous version, have now been correspondingly added in Supplementary Fig. 11j and Supplementary Fig. 24e, which show the terminal spectra features reflect the intrinsic behavior, respectively.

With these experimental data and additional theoretical calculations and analysis, we sincerely hope the referee may find the concerns have been fully addressed.

To address these important issues, we have added descriptions in the end of Supplement Section 13: *“As shown in Supplementary Fig. 24l, 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. 24l is replotted from the spectra in Supplementary Fig. 23j of the CPHN 1 (Supplementary Fig. 23g), from the same CPHN 1 segment as in Supplementary Fig. 24a,e. The observed near-E_F QWS-dependent spectral features on the positive-bias side of the terminals on Br/Ag(111) (Supplementary Fig. 24l) 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.”*

We have also added the caption for the newly added panel in Supplementary Fig. 24l, and followed by a description *“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.”*



Supplementary Fig. 24

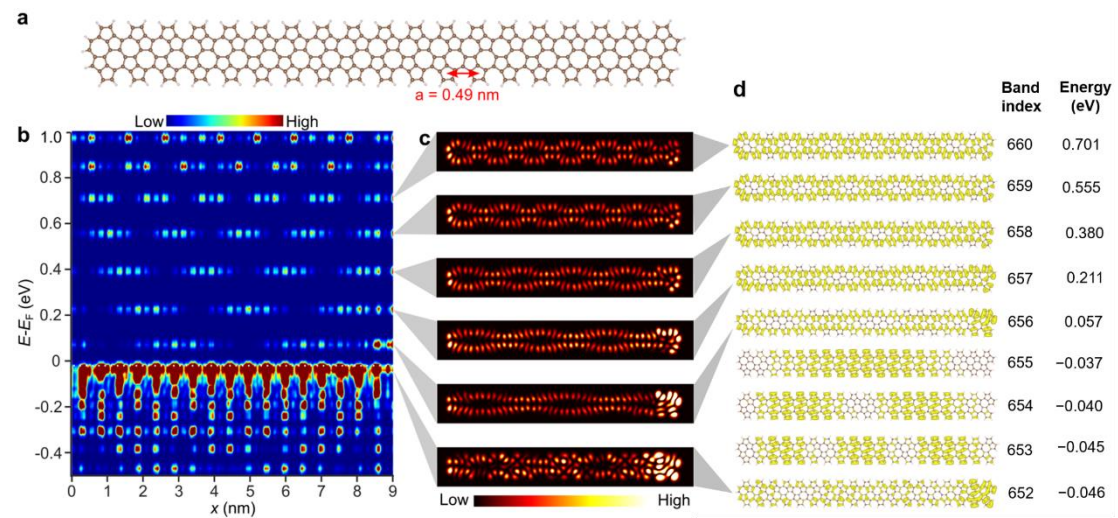


Fig. R1 | State-resolved LDOS analysis of finite CPHN 1. **a-c**, From Extended Data Fig. 8 for the finite CPHN 1. **d**, Calculated QWS wavefunctions of the near- E_F bands, with labelled band indices. The calculated bands from 652-655 are nearly energetically degenerate. All of these near- E_F bands are spatially delocalized though with a certain higher density at the right terminal. These features can be well attributed to the QWS origin.

Band-edge assignment and internal consistency

There are also inconsistencies in the assignment of band edges. The authors consistently assign the energy range around -0.1 to -0.2 eV as the onset of the conduction band for CPHN1 (for example in Supplementary Fig. 23d and Fig. 24d), but this assignment does not appear to be clearly justified by the presented data. Moreover, applying the same assignment procedure to Supplementary Fig. 25d would lead to the conclusion that CPHN2 is metallic, which contradicts the authors' own interpretation. This indicates a lack of internal consistency in the analysis.

Response: We thank the referee for this careful point. We clarify that the band-edge assignment is not based solely on the parabolic FT-LDOS fits—which are only approximate guides. Instead, it relies on the real-space STS QWS sequence: for CPHN 1, the first-envelope QWS of the B_1 manifold is observed below E_F , showing that the manifold crosses E_F ; for CPHN 2, the corresponding first unoccupied QWS lies above E_F with no occupied continuation, consistent with a gap. Thus, applying the same combined criterion does not assign metallicity to CPHN 2. We have added a clarifying statement in Supplementary Section 13 to prevent any misinterpretation of the fits.

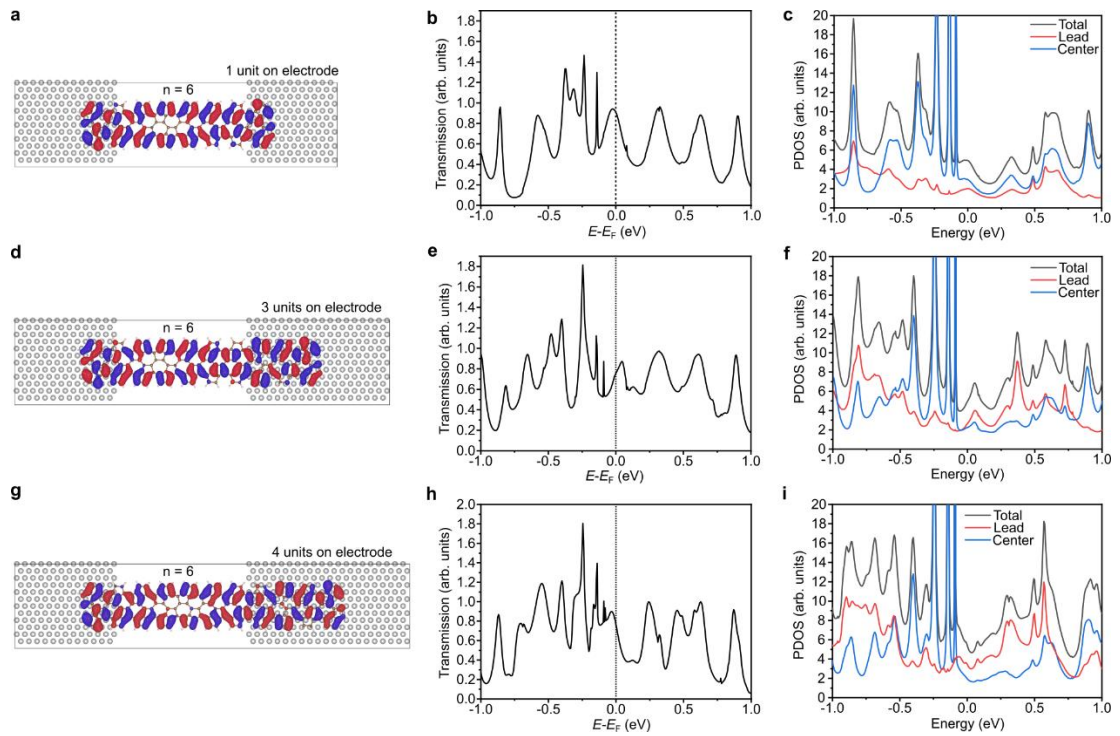
To avoid ambiguity, we have revised the Supplementary Information to state explicitly that the parabolic fits provide only approximate reference values and should not be used alone to assign band edges. We added the following clarification in Supplementary Section 13: *“The assignment of the band onset 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 B_1 -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.”*

Additional experimental requirements

To clarify the electronic structure, it would be important to provide STS spectra over a wider energy range, extending down to approximately -1.0 eV for the intercalated CPHNs, in order to verify that the gap positions are indeed around -0.8 eV and -0.6 eV for CPHN1 and CPHN2, respectively. In addition, more direct and systematic evidence is needed to support the proposed Fermi-level pinning mechanism, for example through comparative measurements under different junction conditions.

Response: We thank the referee for the suggestions. (1) We agree that wider-range spectra

could provide additional detail, but our central metallicity assignment does not require them—it rests on the near- E_F QWS sequence (real-space STS + FT-LDOS/QPI) showing that the B_1 manifold crosses E_F in CPHN 1, while CPHN 2 remains gapped. We have therefore moderated the fitted band-edge values, describing them only as approximate guides. (2) Regarding Fermi-level pinning, we have moderated the wording to a "possible contact-induced level/resonance alignment". Following the suggestion, we have added transport calculations with varying electrode overlap (new Supplementary Fig. 19 and the descriptions added in Section 9), which show a near- E_F resonance across different geometries. We explicitly state this as a plausible explanation, not a unique proof, as the exact position may depend on junction details.



Supplementary Fig. 19 | Transport calculations for CPHN 1 junctions with different electrode-overlap lengths.

Conclusion

While the system under study is interesting and the experimental effort is evident, the manuscript does not yet provide sufficiently controlled structures, rigorous statistical analysis, or internally consistent electronic interpretation to support its central claims. In particular, the conclusion of intrinsic metallicity is not convincingly demonstrated. I therefore cannot recommend publication in Nature.

Response: We thank the referee for the overall assessment. We have revised the manuscript to address all concerns: (1) statistics are now updated with conservative criteria, clearly distinguishing structural assignability from long-segment suitability; (2) we explicitly separate finite-size QWS effects from intrinsic band structure, and clarify that band-edge assignments rely on combined real-space STS and FT-LDOS/QPI sequences, not on parabolic fits alone; (3) the transport interpretation is moderated to a plausible contact-induced level alignment, supported by additional calculations with varied electrode overlap. These changes provide a clearer, internally consistent basis for concluding intrinsic metallicity in the long-ribbon limit, while candidly acknowledging current synthesis and finite-size limitations. We believe the revised manuscript now meets the expected clarity and rigor.

Referee #3 (Remarks to the Author):

This is the review for the latest version of the MS "Narrow carbon pentaheptite nanoribbon as a covalent metal". I was satisfied with the previous revision of the MS, which in my opinion convincingly demonstrates the synthesis of a novel family of GNRs, using a very surprising and interesting synthesis route. Even though the yield is not very high and there is room for improvement in terms of sample quality, to me it seems sufficient to claim that the synthesis pathway works in principle (given that the AFM images Fig. 2c,e shows defect-free segments of 20+ unit cells) and to assess the basic bulk electronic properties of the GNRs.

The experimental line spectra and their FFTs in my opinion show convincingly that for CPHN1 the CB-derived quantum well states in finite segments span across the Fermi level, while they remain above Fermi for CPHN2, indicating that the former should be intrinsically metallic in the limit of very long/infinite ribbons. While the spectra are not perfect and there might be additional features that cannot be assigned with complete certainty, this metallicity would correspond to the predicted behaviour and the FFTs fit well with the authors' simulations.

I have also seen the new set of comments from reviewers #2 and #4 and was asked to briefly comment on them as well.

Response: We thank the referee for the supportive assessment and for acknowledging the synthetic novelty and the FT-LDOS/QPI evidence. In response to the additional comments from reviewers #2 and #4, we have further revised the manuscript to clarify the distinction between finite-size QWS quantization and intrinsic metallicity, and to moderate the quantitative analyses (e.g., parabolic fits) and the transport interpretation. These changes are detailed in our responses below.

Structural quality and statistical analysis: I agree that there is room for improvement in terms of quality and yield of the synthesized ribbons. In particular high-profile publications of novel

GNRs mostly demonstrate significantly better yield and structural quality. However, once one broadens the scope a bit and looks at recent high-impact studies of other carbon nanostructures by on-surface synthesis, the results in the current MS are in line with other publications in the field. E.g., the first publication on the OSS of cyclocarbon (Science 2019) had a yield of less than 20%, if I remember correctly. Some recent high-profile publications of 2D networks based on carbon nanostructures showed only a few defect-free unit cells with low long-range structural coherence (this statement is not meant as a criticism of said papers), see e.g., Science 384, 895 (2024).

Response: We thank the referee for the balanced assessment and for putting our yield in the broader context of challenging on-surface syntheses. We agree that the current quality/yield does not yet match the best-established GNR systems. We have therefore revised the statistics with more conservative criteria: total CPHN 1/2 yield is now 16.7%, and well-defined segments containing at least six repeat units account for ~13.5%. The revised text clearly distinguishes structural assignability from suitability for electronic characterization, while maintaining that the synthesis works in principle and provides sufficiently resolved segments for the local measurements reported.

Relation to prior work: I agree that lateral fusion is well-established. However, taking advantage of on-surface skeletal rearrangement to produce purely 5-7 ribbons is novel, and taking the AFM images in Fig. 2, the resulting ribbons seem to be longer and of higher structural quality than those in the two JACS papers. It is true that one could argue that in terms of metallicity, these new ribbons do not constitute a substantive advancement compared to the 2020 Science paper. However, the current MS does demonstrate a very different mechanism to introduce metallicity, and in my personal opinion, is not less convincing (if not more) than the aforementioned Science paper.

Response: We thank the referee for the balanced assessment. We agree that lateral fusion is established; the key synthetic novelty is the on-surface skeletal rearrangement that yields ribbons composed *exclusively* of 5/7 rings—unlike prior mixed 5/6/7 systems. Regarding the 2020 *Science* paper, we now explicitly acknowledge it but frame our work as a distinct allotropic route to inherent metallicity (controlled by fusion geometry) rather than the first metallic ribbon. We have revised the Abstract and main text accordingly to highlight this difference without overclaiming performance superiority.

Accordingly, in the Abstract we have added: “*Metallic graphene nanoribbons have been realized by band engineering, notably through zero-mode superlattices; however, atomically precise metallic nanoribbons of fully non-benzenoid carbon allotropes, such as the theorized metallic carbon pentaheptites, remain unexplored.*”

In the beginning of main text, we added: *“In contrast to zero-mode-superlattice metallic GNRs, carbon pentaheptite offers an allotropic route to inherent metallicity based solely on fused five- and seven-membered rings.”*

Electronic structure and dispersion analysis: I agree that fitting a parabola to three points is not optimal, but in my opinion the simulations show convincingly that the quadratic approximation is valid only for low k -values. I also see the exact values derived from the fits of only minor importance to the MS and its main conclusions. Regarding the distinction between metallicity in the infinite limit and semiconducting due to quantum confinement in finite segments, I do think the manuscript has significantly improved since the first version, but this distinction could indeed be further emphasized.

Response: We thank the referee for the constructive assessment. We agree that the parabolic fits are only approximate guides for low- k curvature and are not central to our conclusions. We now explicitly state this and de-emphasize the fitted values. Following the suggestion, we have also strengthened the distinction between finite-size QWS quantization and intrinsic metallicity in the long-ribbon limit, adding clarifying statements in the main text and Supplementary Section 13.

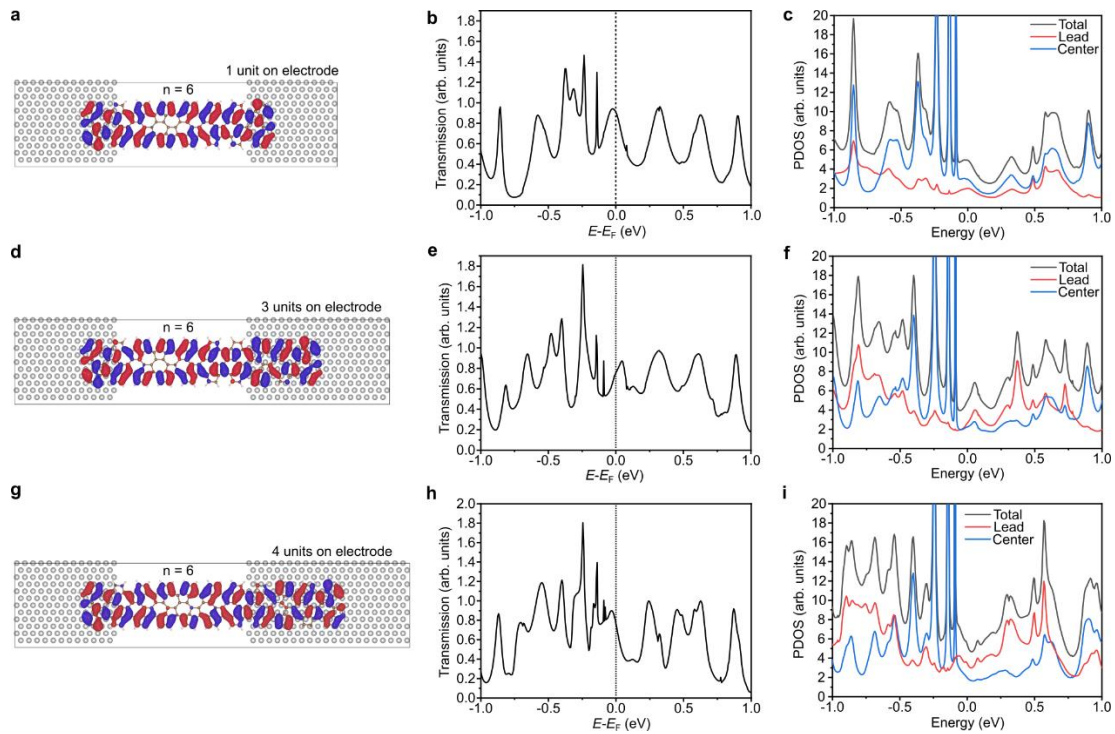
In the main text, we have added: *“Thus, the discrete level spacings observed in finite CPHN I segments reflect quantum confinement and local boundary conditions, rather than a true band gap in the long-ribbon limit.”* In Supplementary Section 13, we have added a corresponding clarification that finite CPHN segments show QWS states whose energies depend on ribbon length, termini and local electrostatic environment, and therefore finite-size level spacings should not be directly interpreted as band gaps of the corresponding infinite ribbon.

Zero-bias peak and Fermi-level pinning: I agree with reviewers 2 and 4 here. The simulations do not really show Fermi level pinning and do not seem to explain well the observed broad peaks around zero bias in the transport measurements. But in my opinion the set-up of the calculations also does not really mimic the experiments. Maybe instead of changing the length of the ribbon, the authors could try a simulation where the ribbon length is constant, but the amount of overlap of the ribbon with one of the leads is changed? This should be a better approximation to the experimental set-up, I would think.

Response: We thank the referee for the constructive suggestion. We agree that the previous calculations did not fully mimic the experiment and do not prove strict Fermi-level pinning. We have therefore moderated the interpretation to a "possible contact-induced near- E_F level

alignment". Following the suggestion, we performed new transport calculations with a fixed six-unit freestanding segment and varied the overlap with the right electrode (new Supplementary Fig. 19). These show a near- E_F B_1 -derived resonance across different overlaps, supporting that charge transfer/hybridization can shift a QWS into the near- E_F region. We now present this as a plausible scenario, not a unique proof, and have replaced the strong "pinning" statement accordingly in the main text.

We have revised the main text accordingly. The previous strong statement on Fermi-level pinning has been replaced by a more conservative description: “Our transport calculations for CPHN 1 adsorbed on two Ag electrodes (Supplementary Figs. 18, 19 and Supplementary Section 9) reveal a near- E_F transmission resonance arising from a B_1 -band quantum well state (QWS), whose wavefunction is spatially extended over the CPHN 1 backbone. The charge transfer and hybridization between the electrodes and CPHN 1 (Extended Data Fig. 6b) can shift and broaden the QWS-derived resonances, providing a plausible contact-induced level-alignment scenario³⁰ for the broad near- E_F conductance enhancement observed experimentally in various CPHN 1 samples (Fig. 2i, Supplementary Figs. 9i,j and 11f).”



Supplementary Fig. 19 | Transport calculations for CPHN 1 junctions with different electrode-overlap lengths.

Unresolved spectral features: To me, the appearance of the discretization gap is in line with previous publications, see e.g., Nat. Comms. 16, 5632 (2025). The features in SFig. 23e look like electronic states in a mixed-valence regime (maybe related to localized states at the non-

perfect ribbon termini), which typically give rise to asymmetric orbital-like features in dI/dV close to/at zero bias, see e.g., Science 309, 1542 (2005) and Nanotechnology 19, 065401 (2008).

Response: We thank the referee for the helpful interpretation and for pointing out relevant analogies in the literature. We agree that the near- E_F discretization/gap-like feature observed in finite CPHN **1** segments is consistent with finite-size QWS quantization and local effects, rather than a true band gap of the infinite ribbon. We have clarified this point in Supplementary Section 13 by noting that finite-size QWS quantization, local electrostatic environment and possible addition-energy effects can enlarge the apparent near- E_F level spacing in finite segments.

Regarding the features in the terminal spectra, we also appreciate the referee's suggestion that localized states associated with non-ideal termini could contribute to the local line shapes. To examine this issue more clearly, we have revised Supplementary Fig. 24 by adding reference spectra from the ribbon interior in Supplementary Fig. 24l, together with background spectra from the Br/Ag(111) substrate in Supplementary Fig. 24e. Comparison of the terminal-site spectra with the interior spectra shows that the terminal features mainly arise from the tails of QWS signals, rather than from asymmetric Fano-like zero-bias peaks. The added reference spectra also show that no robust zero-energy peak pinned at E_F is observed at the terminals.

We do not exclude that localized terminal defect states may contribute to some of the terminal-site spectra, depending on the specific terminal structure. However, these possible terminal states do not produce an assignable zero-bias peak either on Ag(111) (Supplementary Fig. 11j,k) or on Br/Ag(111) (Supplementary Fig. 24e,l). Therefore, they cannot account for the broad near-zero-bias conductance enhancement observed in the contact-transport measurements (Fig. 2i and Supplementary Figs. 9i,j and 11f). In the revised manuscript, we instead assign this transport feature more conservatively to a near- E_F transmission resonance arising from a B_1 -band QWS, plausibly through a contact-induced level-alignment scenario.

Accordingly, we have revised the caption of Supplementary Fig. 24 to clarify the purpose of these spectra and to state that no robust zero-energy peak pinned at E_F is observed. The main electronic assignment remains based on the dispersive QWS patterns recorded along the ribbon interior and their comparison with finite-length and periodic calculations.

Band-edge assignment and internal consistency: Here I think I disagree with the reviewers. If I was given just the experimental dI/dV line spectra and their FFTs and nothing else; no theory, no predictions, I would make the same qualitative assignment regarding the position of the conduction bands (crossing Fermi vs not crossing Fermi) as the authors. Given the dispersion of the quantized states and the distribution of their lobes, this seems to me the most sensible interpretation. The data are not perfect, there might be additional features that are not fully understood, especially related to additional states localized at the defective ribbon ends, but to

me that does not necessarily invalidate the characterization of the bulk electronic properties based on the line spectra above the ribbon interior.

Response: We thank the referee for the supportive assessment. We agree that the qualitative assignment—based on the QWS dispersion and real-space lobe distribution—is the most sensible interpretation, independent of the parabolic fits. To enhance clarity, we now state explicitly in Supplementary Section 13 that the band-edge assignment relies on the combined real-space STS and FT-LDOS sequences, not on fits alone; fits serve only as approximate curvature guides. We also clarify that local terminal features, while not fully assigned, do not affect the bulk assignment derived from interior spectra.

We have added the following clarification to Supplementary Section 13: *“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.”*

Referee #4 (Remarks to the Author):

I co-reviewed this manuscript with one of the reviewers who provided the listed reports.

Response: We thank Referee #4 for the evaluation of our work.

Referees' comments:

Referee #3 (Remarks to the Author):

This is the review for the revised version of the manuscript "Narrow carbon pentaheptite nanoribbon as a covalent metal" by Huang and co-workers.

The authors refined the statistical analysis of the synthesis yield, did another set of transport calculations to investigate the origin of the broad zero-bias feature in the lifting experiments, and modified the text to put the manuscript into context of related works and to add some qualifiers and clarify some of the interpretations, thereby addressing all the points raised in the previous round of reviews. The main results are unaffected by these changes, and as I stated in my previous report, I find the conclusions regarding the crossing of the Fermi energy by the CB and thus the metallicity convincing, as well as the new revisions.

Response: We are grateful to the referee for the favorable evaluation of our revised manuscript.

This being said, having seen Fig. R1 and new Fig. S19, I do have two final comments:

#1: In Fig. R1, panel d shows the wave functions of the QWS around the Fermi energy for a finite metallic (in the infinite limit) ribbon. Based on their shape and symmetry, bands 660 to 656 clearly belong to the same, upward dispersing band, which seems to be crossing Fermi. However, I am quite puzzled by bands 655 to 653, which – based on their shape and symmetry – seem to form a distinct set of QWS derived from a downward dispersing band. Do the authors have any insights on the nature or origin of these states? If they arise from the VB, then would that suggest some kind of band inversion?

Response: We thank the referee for this careful observation and apologize for the lack of clarity regarding the states in bands 655–653 of Fig. R1.

To directly address their origin: these states arise from band folding induced by the finite length of the CPHN 1 ribbon. Specifically, they correspond to the folded branches of the B_2 states near the Fermi energy in real space. As demonstrated by the dashed lines in **Supplementary Fig. 29e** (the previous Supplementary Fig. 28e), the band folding of both B_1 and B_2 generates similar folded patterns, which can indeed appear as a downward-dispersing feature. However, this is purely a folding artifact and does not represent a genuine downward-dispersing band.

Therefore, the apparent downward dispersion in QWS real-space feature is not physically associated with the VB.

#2: The authors made another set of transport calculations, Fig. S19, based on a comment of

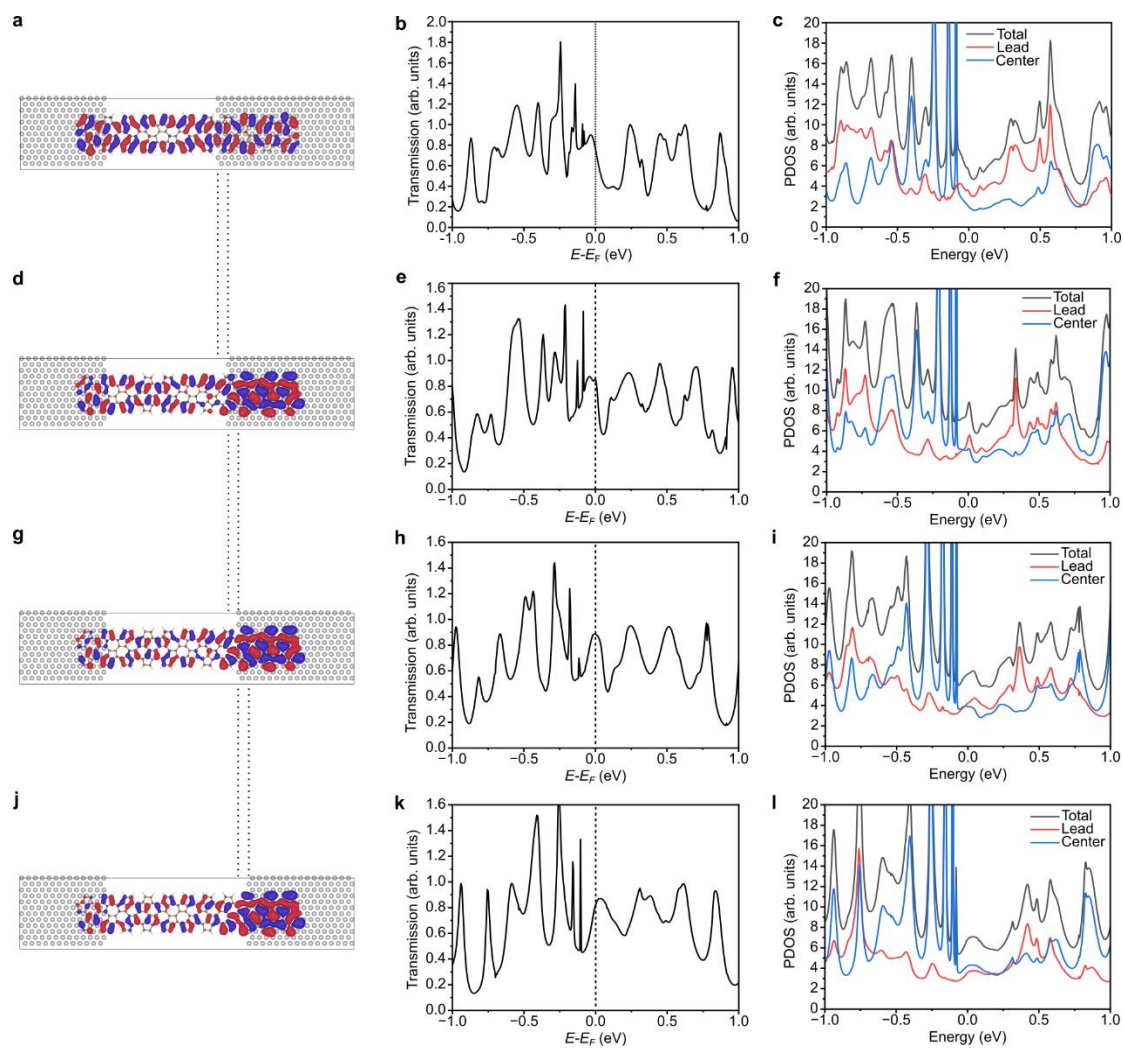
mine in my previous report, and I very much appreciate the authors efforts. However, I think there was a misunderstanding about my idea. In their new calculations, the authors still change the total length of the ribbon, such that even though the overlap of one ribbon end with the lead increases, the length of the free-standing segment stays the same.

My idea was to keep the total length constant but change the amount of overlap of one of the ends with its lead, such that the free-standing segment gets longer while segment coupled to the lead get shorter. That is my somewhat naïve experimentalist idea of how the calculations would best mimic the experiment, where I-Vs are measured while the ribbon is step-by-step delaminated from the surface by the tip. But I have to admit that I have no idea if that would yield anymore insights than the previous calculations. I also do not know how expensive these kind of calculations are, and I am in principle fine with that feature being tentatively assigned to “possible contact-induced level/resonance alignment” (as to me, a lack of definitive explanation of that feature does not weaken the conclusions made based on the dispersion of the CB-derived QWSs).

Response: We thank the referee for this clarification and for their constructive suggestion. We acknowledge that our previous calculations did not fully capture the intended geometry, as they kept the free-standing segment fixed while varying the total ribbon length.

In response to the referee's specific proposal, we have now performed new transport calculations in which the total ribbon length is held constant, while the overlap with one electrode is varied, consequently altering the length of the free-standing segment. The results have been added in **Supplementary Fig. 20**, and the corresponding discussion in Supplementary Section 9 has been revised accordingly. In these updated calculations, a QWS-derived resonance still appears in the vicinity of the E_F , despite energetic position shifts slightly with the overlap that may change the charge transfer at the ribbon–electrode interface. We note that analogous peak shifts are observed in our experimental data (Fig. 2i and Supplementary Figs. 9i,j and 11f), lending support to our assignment of this feature to contact-induced level/resonance alignment.

We also appreciate the referee's insightful comments that a definitive explanation of this particular feature is not required for the overall robustness of our findings, and we agree that the current interpretation sufficiently addresses the observed behavior without overextending our claims.



Supplementary Fig. 20 | Transport calculations for CPHN 1 junctions with a fixed total ribbon length and varying electrode-overlap lengths.