Engineering of robust topological quantum phases in graphene nanoribbons

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Boundaries between distinct topological phases of matter support robust, yet exotic quantum states such as spin–momentum locked transport channels or Majorana fermions1–3. The idea of using such states in spintronic devices or as qubits in quantum information technology is a strong driver of current research in condensed matter physics4–6. The topological properties of quantum states have helped to explain the conductivity of doped trans-polyacetylene in terms of dispersionless soliton states7–9. In their seminal paper, Su, Schrieffer and Heeger (SSH) described these exotic quantum states using a one-dimensional tight-binding model10,11. Because the SSH model describes chiral topological insulators, charge fractionalization and spin–charge separation in one dimension, numerous efforts have been made to realize the SSH Hamiltonian in cold-atom, photonic and acoustic experimental configurations12–14. It is, however, desirable to rationally engineer topological electronic phases into stable and processable materials to exploit the corresponding quantum states. Here we present a flexible strategy based on atomically precise graphene nanoribbons to design robust nanomaterials exhibiting the valence electronic structures described by the SSH Hamiltonian in cold-atom, photonic and acoustic experimental configurations12–14. We demonstrate the controlled periodic coupling of topological boundary states15–17 at junctions of graphene nanoribbons with armchair edges to create quasi-one-dimensional trivial and non-trivial electronic quantum phases. This strategy has the potential to tune the bandwidth of the topological electronic bands close to the energy scale of proximity-induced spin–orbit coupling18 or superconductivity19, and may allow the realization of Kitaev-like Hamiltonians20 and Majorana-type end states21.

The fundamental features of the SSH model—which describes a one-dimensional chain of dimerized, coupled and spinless fermions—are summarized in Fig. 1. Conceptually, its basic elements are an inter-cell coupling $t_n$ between states of neighbouring dimers (Fig. 1a). The corresponding spinor-based Hamiltonian $H(k) = d_k (k) \sigma_x + d_k (k) \sigma_y$ (with $d_z = t_m \cos(k)$ and $d_y = t_m \sin(k)$) leads to the energy spectrum $E(k) = \pm \sqrt{t_m^2 + t_n^2 + 2t_m t_n \cos(k)}$. This dispersion relation yields three extremal phases: (i) an intra-cell decoupled, insulating phase with $E(\pi) = 0$ and $E(0) = \pm 2t_m$, equal coupling strengths $t_n = t_m = 0$; and (iii) an inter-cell decoupled, insulating phase with $E(k) = \pm t_n$ for $t_n = 0$ and $t_m = 0$.

These three extremal solutions of the SSH chain can be smoothly connected by introducing a phase factor $\phi \in [0, \pi/2]$ governing the strength of $t_n$ and $t_m$ via $t_n = \gamma \sin^2(\phi)$ and $t_m = \gamma \cos^2(\phi)$, where $\gamma$ denotes the bandwidth. The corresponding series of band structures $E(k, \phi)$ in Fig. 1b reveals non-dispersive band structures (orange) for the two insulating chain configurations at $\phi = 0$ and $\phi = \pi/2$, while for $\phi = \pi/4$ (blue) a gapless metallic phase is found. That the smooth transition between two insulating phases can only occur by closing the gap is clear evidence of their distinct topological class. This class can be assigned using the winding number of $\tau(k, \phi) = (d_z (k, \phi), d_y (k, \phi))$ around the origin as a $\mathbb{Z}_2$ topological invariant11, which is $\mathbb{Z}_2 = 1$ for $\phi < \pi/4$ and $t_n < t_m$, making the corresponding phases topologically non-trivial, and topologically trivial with $\mathbb{Z}_2 = 0$ for $\phi > \pi/4$ and $t_n > t_m$.

Unfortunately, the winding number cannot be directly determined in experiments. However, the bulk–boundary correspondence, that is, the relation between the bulk winding number and the existence or absence of boundary states, offers a convenient experimental approach with which to determine a topological class. In the energy spectrum of a finite SSH chain of 25 dimers (Fig. 1c) the topologically non-trivial phases for $\phi < \pi/4$ can readily be distinguished from the trivial ones with $\phi > \pi/4$ by the presence of two degenerate zero-energy states localized at the chain ends.

Specifically designed graphene nanoribbons (GNRs) provide a platform with which to realize a class of robust solid-state nanomaterials that can flexibly encompass all three of the abovementioned quantum phases of the SSH chain. The atomically precise structural control required to rationally engineer the corresponding electronic structures can be achieved by on-surface synthesis22. Since the first successful bottom-up synthesis of GNRs by polymerization of dedicated molecular precursors15, a wide variety of GNRs exhibiting different width, chirality, edge structure and chemical doping has been realized16,17. The chemical robustness of GNRs allows their handling under ambient conditions23 and their integration into high-performance electronic nanodevices24, promising a technological exploitation of GNR-based topological quantum phases18.

The ability to flexibly engineer SSH-like topological quantum phases in GNRs requires a suitable electronic state representing $|\psi\rangle$. We identify such a state in the zero-energy boundary state at the junction of two armchair graphene nanoribbons (N-AGNR) of different widths. Here $N$ denotes the number of transverse carbon atom rows15. The boundary state we are considering here is itself of topological origin18. To understand this, we consider that N-AGNRs can be classified into three families according to their electronic properties. For $N = 3p$ and $N = 3p + 1$ (where $p$ is an integer) the corresponding AGNRs exhibit a gapped electronic structure, whereas for $N = 3p + 2$ a gapless (that is, metallic) behaviour is observed at the tight-binding level of theory25. At a smooth junction between a gapped N-AGNR with $N = 3p + 1$ and a gapped $N = 3p + 3$ AGNR (that is, with two additional rows of carbon atoms) (see Supplementary Figs. 1–4), a zero–energy boundary state occurs owing to the gapless $N = 3p + 2$ intermediate (Supplementary Figs. 5–9). This situation is analogous to polyacetylene, where the smooth transition from one bond alternation pattern to the complementary one can only proceed via closure of the gap, leading to a zero–energy soliton state8,11. The wavefunction of the corresponding boundary state at a 7-AGNR/9-AGNR junction is displayed in Fig. 1d.

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Creating a periodic sequence of such boundary states along and across the N-AGNR backbone, by local extension to a finite (N + 2)-AGNR segment (Fig. 1e), produces an effective solid-state analogue of a cis-SSH chain. Here, the index n denotes the length of the (N + 2)-AGNR segment and m corresponds to the separation between the opposite segments across the backbone. The resulting staggered (S) ribbon structure is labelled N-AGNR-(n,m). Thereby, the structure shown in Fig. 1e and Fig. 2b with N = 7, n = 1 and m = 3 is denoted as 7-AGNR-S-(1,3) (see Supplementary Figs. 1–4 for details). In terms of the SSH Hamiltonian, n is directly related to the intra-cell coupling $t_n$ while m determines the inter-cell coupling $t_m$.

The tight-binding bulk band structure of the staggered 7-AGNR-S-(1,3) is compared to the band structure of the pristine 7-AGNR backbone in Fig. 2. The appearance of four dispersive bands around the Fermi energy of the 7-AGNR backbone structure is readily observed (see also Supplementary Figs. 10 and 11). These bands are in excellent agreement with the zone-folded SSH energy spectrum $E(k)$ (blue solid lines in Fig. 2b) with $t_n = 0.45 \text{ eV}$ and $t_m = 0.59 \text{ eV}$.

We present a synthetic design to experimentally realize the staggered 7-AGNR-S-(1,3) structure by using 6,11-bis(10-bromoanthracen-9-yl)-1,4-dimethyltetraacene (BADMT, monomer 1) as precursor monomer. The methyl groups can form zigzag edges smoothly bridging the 7- and 9-AGNR segments via cyclization with the neighbouring aromatic rings, forming the intermediate 8-AGNR structure. The corresponding on-surface synthesis route (Fig. 2c) consists of the sublimation of monomer 1 onto a clean Au(111) surface, subsequent thermal precursor activation (dehalogenation) and polymerization at 200°C, and finally cyclohydrogenation of the polymer at 400°C. A constant-height non-contact atomic force microscopy (nc-AFM) image of the resulting structure is shown in Fig. 2d. The chemical stability of this GNR was investigated by Raman spectroscopy (Supplementary Fig. 27), and no spectral changes were detected after 5 days under ambient conditions, consistent with the high stability of the pristine backbone 7-AGNR.

STS investigation reveals that the 2.4-eV bandgap of the pristine 7-AGNR on Au(111)26–27 is drastically reduced to 0.65 ± 0.1 eV for the 7-AGNR-S-(1,3). Constant-current $I(V)$ maps of the main spectroscopic features around the gap (Fig. 2e) can be reliably assigned to the bottom and the top of the valence band (VB) and conduction band (CB), respectively, by comparison with tight-binding simulations (Fig. 2f). The experimentally observed total bandwidth $\Delta E_{\text{exp}} = 1.6 \text{ eV}$ (VB minimum to CB maximum, see Supplementary Figs. 15, 17) is in good agreement with the one found from the tight-binding calculations $\Delta E_{\text{calc}} = 2\sqrt{t_n^2 + t_m^2} + 2t_n = 2.08 \text{ eV}$ with $t_n = 0.45 \text{ eV}$ and $t_m = 0.59 \text{ eV}$. From density functional theory (DFT, Supplementary Fig. 12) we deduce $\Delta E_{\text{DFT}} = 1.95 \text{ eV}$ with $t_n = 0.37 \text{ eV}$ and $t_m = 0.60 \text{ eV}$. The symmetry of $E(k)$ with regard to exchange of $t_n$ and $t_m$ does not allow us to determine which coupling term prevails and it remains an open question whether the 7-AGNR-S-(1,3) structure belongs to the topologically non-trivial class ($Z_2 = 1$ with $t_m > t_n$) or the topologically trivial class ($Z_2 = 0$ with $t_m < t_n$).

To clarify this question we exploit the bulk–boundary correspondence11 and check for the presence of end states at the termini of the N-AGNR-(n,m) nanoribbon family. There is, however, a complication arising from the concomitant presence of zigzag termini related end states of the N-AGNR backbone.28 Both types of end states have topological origins but of different nature. As detailed in Supplementary Figs. 18–20, these two states can interact and hybridize such that the SSH end state is no longer present at zero energy. To prevent this, the terminus of the N-AGNR-(n,m) needs to be extended by a sufficiently long segment of pristine N-AGNR backbone, as illustrated in Fig. 3a and b. The resulting local density of states (LDOS) at the end of...
Fig. 2 | Electronic structure of the staggered edge-extended 7-AGNR-S(1,3) nanoribbon. a, b, Structural models and tight-binding band-structure diagrams for the pristine 7-AGNR backbone (a) and the staggered 7-AGNR-S(1,3) (with $\gamma_0 = 3$ eV) (b). The thickness of the lines and the colour—black (higher) to brown (lower)—denote the magnitude of $|\langle k | \psi_n(k) \rangle|$, that is, the projection of the electronic states onto free electron states (Brillouin zone unfolding). Solid blue lines in b denote the analytical bands of the cis-SSH chain. c, Schematic representation of the on-surface synthesis route from monomer 1 to 7-AGNR-S(1,3). d, Constant-height nc-AFM image (with CO-functionalized tip) of the frequency shift $\Delta f$ of a 7-AGNR-S(1,3) segment on Au(111). e, Series of constant-current $dI/dV$ spectra of the GNR shown in d at selected energies close to the Fermi energy, $E_F$ (which corresponds to 0 V sample bias). The set-point currents are 300 pA (with $U = -0.6$ V bias), 600 pA ($U = -0.05$ V), 800 pA ($U = 0.65$ V) and 1 nA ($U = 0.9$ V). f, Sequence of tight-binding-derived constant-height charge-density maps at the VB and CB extrema (at $-1$ eV, $-0.2$ eV, +0.2 eV and +1.0 eV from bottom VB to top CB). The 1 nm scale bar in d applies to all maps d–f.

The $N$-AGNR-S($n,m$) segment (indicated by the arrows) as a function of $m$ is shown in Fig. 3a and b for the 7-AGNR-S(1,m) and 7-AGNR-S(3,m) nanoribbon families, respectively. The $(m = 1)$ 7-AGNR-S(1,1) exhibits a zero-energy end state, indicating that it belongs to the topologically non-trivial phase ($\phi < \pi/4$) with $t_0 = t_{m}$. Increasing $m$ decreases $t_m$ while $t_0$ remains approximately constant ($n = 1$). For $m = 2$ the LDOS shows a closing of the gap corresponding to $t_0 \approx t_{m}$ ($\phi \approx \pi/4$), thus marking the metallic intermediate separating the non-trivial 7-AGNR-S(1,1) from the trivial 7-AGNR-S(1,3), which shows a gap again but with no zero-energy end states. For $n = 3$ (Fig. 3b), $t_0$ is reduced and the non-trivial to trivial transition with $t_0 \approx t_{m}$ should occur at larger $m$ (that is, smaller $t_m$) than in the $n = 1$ case. As can be seen from Fig. 3b, zero-energy end states do indeed occur for $m = 1, 2$ and 3, indicating that, according to the tight-binding calculations, the experimentally realized 7-AGNR-S(1,3) belongs to the topologically trivial $Z_2 = 0$ class.

To verify this finding experimentally, the synthetic route shown in Fig. 2 was modified to allow the required extension of the staggered nanoribbon structure with a pristine 7-AGNR backbone segment. This is realized by sequential deposition of monomer 1 for the 7-AGNR-S(1,3) and dibromo-bianthryl (DBBA, monomer 2) for the 7-AGNR (Fig. 3c, Supplementary Fig. 25). Differential conductance
Fig. 4 | Non-trivial topological (Z₂ = 1) phase of the inline edge-extended 7-AGNR-I(1,3) structure. a, On-surface synthesis route to the 7-AGNR backbone extended 7-AGNR-I(1,3) nanoribbon. b, LDOS plots evaluated at the end of the 7-AGNR-I(1,m) segment (see arrow in a) as a function of inter-segment spacing m, revealing the Z₂ = 1 to Z₂ = 0 transition at m = 4 with nearly complete gap closure and disappearance of the zero energy states for m > 3. d, Constant-height nc-AFM frequency shift (Δf) image of a 5-unit 7-AGNR-I(1,3) segment with 7-AGNR extensions at both ends. c, dl/dV spectra (−0.6 V and 100 pA set-point before opening feedback loop) taken at the locations indicated by the markers of corresponding colour in d, e. Experimental dl/dV maps of the main spectroscopic features at +0.15 V, +0.25 V and +0.7 V (all with I = 500 pA). f, Tight-binding-simulated charge-density maps at the top of the VB, at E = 0 eV, and at the bottom of the CB, computed for the experimental structure (d). The 1 nm scale bar in d applies also to panel e and f.

dl/dV spectroscopy at the end of the SSH GNR segment (red curve and marker in Fig. 3d and e) and at the internal SSH chain site (blue) shows nearly identical spectra with no indication of an end state. This is further corroborated by dl/dV mapping at selected energies around E = 0 eV (Fig. 3f). At U = −0.05 V the onset of the spatially extended VB states of the 7-AGNR-S(1,3) can be seen; U = 0.25 V corresponds to a gap with no particular features, and at +0.65 V the bottom of the CB can be observed, in good agreement with the tight-binding charge-density simulation of the lowest-energy CB state of the 7-AGNR−7-AGNR-S(1,3) heterostructure (Fig. 3g). The experiment therefore confirms the tight-binding prediction that the 7-AGNR-S(1,3) is topologically trivial with Z₂ = 0.

The staggered N-AGNR-S(n,m) exhibits boundary states only for nanoribbon widths N = 3p + 1 (where p is an integer) and provides an electronic cis-polyacetylene analogue. If instead of an asymmetric N-AGNR to (N + 2)-AGNR junction an axially symmetric N-AGNR to (N + 4)-AGNR junction is considered, as illustrated in Fig. 4a, the resulting ‘in-line’ edge-extended GNR will yield zero-energy boundary states for all backbone widths N (Supplementary Fig. 6). Similar to the staggered structure, the (N + 4) segment length is denoted by n and the segment spacing by m, and the in-line ‘I’ structure is thus labelled N-AGNR-I(n,m). The structure shown in Fig. 4a is therefore a 7-AGNR-I(1,3). The LDOS series for the 7-AGNR-I(1,m) family in Fig. 4b reveals topological end states for m = 2 and m = 3 with the non-trivial to trivial phase transition between m = 3 (Z₂ = 1) and m = 4 (Z₂ = 0). The bulk band structure for the 7-AGNR-I(1,3) exhibits two trans-polyacetylene-like bands with τb = 0.45 eV and τt = 0.65 eV (Supplementary Fig. 11), which is very similar to 7-AGNR-S(1,3).

Topological phase diagrams for the 7-AGNR-S(n,m) and 7-AGNR-I(n,m) structures are given in Supplementary Fig. 14 for n ∈ [1, 9] and m ∈ [1, 9]. The synthetic route to the 7-AGNR extended 7-AGNR-I(1,3) structure is analogous to the one for the staggered structure, but using 6,13-bis(10-bromoanthracen-9-yl)-1,4,8,11-tetramethylpentacene (BATMP, monomer) as the precursor molecule. Figure 4d presents the nc-AFM image of a 5-unit 7-AGNR-I(1,3) that is extended by 7-AGNR segments at both ends. dl/dV spectra recorded at the 7-AGNR/7-AGNR-I(1,3) junction (dark blue and red in Fig. 4c and d) reveal a state at approximately 0.25 V that is only present at the chain ends, as confirmed by dl/dV mapping (Fig. 4e). Comparison with tight-binding calculations (Fig. 4f) reveals that the extended state at 0.15 V can be assigned to the top of the VB, the 4-lobe state at +0.7 V in the centre of the chain to the CB minimum, and that the state at +0.25 V is indeed the expected topologically non-trivial bulk-boundary end state (see Supplementary Fig. 26 for a high-resolution dl/dV map).

This state is not observed at exactly 0 V owing to charge doping by the substrate, which is well known to occur for low-bandgap GNRs on Au(111) and its non-mid-gap position might be due to substrate-dependent many-body energy renormalization. All together, this analysis shows that, in contrast to the staggered trivial 7-AGNR-S(1,3), the inline edge-extended 7-AGNR-I(1,3) belongs to the topologically non-trivial Z₂ = 1 class and hosts topological end states.

For our discussion we have chosen the topological invariant related to the winding number of the SSH model (Z₂) as identifier of the topological class. Alternatively, the Zak phase of all occupied bands can also be used, yielding the topological invariant \( Z_{\phi} \), which is \( Z_2 = 1 - Z_{\phi} \) for the structures considered here (see Supplementary Fig. 13).

The presence of short zigzag edge segments in the structure families discussed here suggests the possibility of magnetic ordering. For the 7-AGNR-S(1,3) and 7-AGNR-I(1,3) structures the relatively strong coupling suppresses magnetic ordering, but the formation of antiferromagnetic spin-chains is expected for structures with larger \( n \) and \( m \) (Supplementary Figs. 22–23). A direct effect of the (n,m)-dependent coupling strength is that the bandgap can be tuned over a wide range without changing the ribbon width (Supplementary Fig. 14).

Online content

Any Methods, including any statements of data availability and Nature Research reporting summaries, along with any additional references and Source Data files, are available in the online version of the paper at https://doi.org/10.1038/s41586-018-0375-9.

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1. Hasan, M. Z. & Kane, C. L. Topological insulators. Rev. Mod. Phys. 82, 3045–3067 (2010).
2. König, M. et al. Quantum spin Hall insulator state in HgTe quantum wells. Science 318, 766–770 (2007).
3. Kitagawa, S., Nakamura, T., Ishii, A. & Ando, H. Unpaired Majorana fermions in quantum wires. Phys. Usp. 44, 131–136 (2001).
4. Bradlyn, B. et al. Topological quantum chemistry. Nature 547, 298–305 (2017).
5. de Vries, E. K. et al. Towards the understanding of the origin of charge-current-induced spin voltage signals in the topological insulator Bi₂Se₃. Phys. Rev. B 92, 201102 (2015).
6. Mourik, V. et al. Signatures of Majorana fermions in hybrid superconductor-semiconductor nanowire devices. Science 336, 1003–1007 (2012).
7. Chiang, C. K. et al. Electrical conductivity in doped polyacetylene. *Phys. Rev. Lett.* **39**, 1098 (1977).

8. Su, W.-P., Schrieffer, J. R. & Heeger, A. J. Soliton excitations in polyacetylene. *Phys. Rev. B* **22**, 2099–2111 (1980).

9. Longuet-Higgins, H. C. & Salem, F. R. S. L. The alternation of bond lengths in long conjugated chain molecules. *Proc. R. Soc. Lond. A* **251**, 172–183 (1959).

10. Su, W., Schrieffer, J. R. & Heeger, A. J. Solitons in polyacetylene. *Phys. Rev. Lett.* **42**, 1698 (1979).

11. Asbóth, J. K., Orozslányi, L. & Pályi, O. A short course on topological insulators: band-structure topology and edge states in one and two dimensions. *Lecture Notes in Physics* Vol. 919 (Springer, Cham, 2016).

12. Meier, E. J., An, F. A. & Gadway, B. Observation of the topological soliton state in the Su–Schrieffer–Heeger model. *Nat. Commun.* **7**, 13986 (2016).

13. Tan, W., Sun, Y., Chen, H. & Shen, S.-Q. Photonic simulation of topological excitations in metamaterials. *Sci. Rep.* **4**, 3842 (2015).

14. Chen, B. G.-g., Upadhyaya, N. & Vitelli, V. Nonlinear conduction via solitons in a topological mechanical insulator. *Proc. Natl Acad. Sci. USA* **111**, 13004–13009 (2014).

15. Cai, J. et al. Atomically precise bottom-up fabrication of graphene nanoribbons. *Nature* **466**, 470–473 (2010).

16. Nguyen, G. D. et al. Atomically precise graphene nanoribbon heterojunctions from a single molecular precursor. *Nat. Nanotechnol.* **12**, 1077–1082 (2017).

17. Talirz, L., Ruffieux, P. & Fasel, R. On-surface synthesis of atomically precise graphene nanoribbons. *Adv. Mater.* **28**, 6222–6231 (2016).

18. Su, W.-P., Schrieffer, J. R. & Heeger, A. J. Soliton excitations in polyacetylene. *Phys. Rev. B* **22**, 2099–2111 (1980).

19. Wang, S. et al. Giant edge state splitting at atomically precise graphene zigzag edges. *Nat. Commun.* **7**, 11507 (2016).

20. Kimouche, A. et al. Ultra-narrow metallic armchair graphene nanoribbons. *Nat. Commun.* **6**, 10177 (2015).

21. Merino-Díez, N. et al. Width-dependent band gap renormalization in substrate-supported graphene nanoribbons. *J. Phys. Chem. Lett.* **7**, 1526–1533 (2016).

22. Fujita, M., Wakabayashi, K., Nakada, K. & Kusakabe, K. Peculiar localized state at zigzag graphene edge. *J. Phys. Soc. Jpn* **65**, 1920–1923 (1996).

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Author contributions O.G., P.R. and R.F. conceived and supervised this work. A.N., X.Y., X.F. and K.M. designed and synthesized the molecular precursors. S.W. performed the on-surface synthesis and scanning probe microscopy characterization. G.B.B. did the Raman analysis, C.D., A.C. and V.M. performed the corresponding simulations. C.A.P. did the DFT calculations. O.G. developed the conceptual framework, performed the tight-binding calculations and wrote the manuscript, with contributions from all co-authors. P.R., S.W. and O.G. designed the figures, with contributions from other co-authors.

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METHODS

Tight-binding calculations of electronic structure. The calculations of the electronic structure are based on the nearest-neighbour hopping tight-binding Hamiltonian considering the $2p_z$ orbital of the carbon atoms only:

$$H = \sum_i \varepsilon_i c_i^\dagger c_i - \sum_{\langle i,j \rangle} \gamma_{ij} c_i^\dagger c_j$$  \hspace{1cm} (1)

Here $c_i^\dagger$ and $c_i$ denote the usual creation and annihilation operators on site $i$. $\langle i,j \rangle$ denotes the summation over nearest-neighbour sites, the on-site energies $\varepsilon_i$ are all set to zero, and the nearest-neighbour hopping parameter is chosen to be $\gamma_0 = 3 \text{ eV}$. Band structures are calculated by taking into account the wave vector-dependent complex Bloch phase factors in the tight-binding Hamiltonian. Unfolding of the band structures into the extended Brillouin zone is achieved by projection of the wavefunctions of energy $E_n$ on plane waves $|\psi_n(k)|$. The corresponding weight is displayed by marker size and colour. Here $k_1$ and $k_2$ denote the wave vectors parallel and perpendicular to the GNR axis, respectively. The perpendicular wave vector $k_2$ for the projection is chosen to be non-zero in order to cut through the Dirac point of the parent graphene structure at $k_2 = \pi / a$ and $k_1 = 2\pi / \sqrt{3}a$ with $a = 2.44 \text{ Å}$ being the length of the graphene basis vector.

Wavefunctions are reconstructed from the tight-binding eigenvectors $\alpha_{\varepsilon_n}$ of energy $E_n$ by summing up the carbon $2p_z$ Slater-type orbitals with $\xi = 1.625$ atomic units over the atomic sites $i$ of the structure.

$$\psi_n(r) = \sum_i \alpha_{\varepsilon_n i} \exp(-\xi |r_i-r|)$$  \hspace{1cm} (2)

STS-mapping simulations are achieved to a first approximation by displaying the charge density of the states considered in the energy interval $[\varepsilon_1, \varepsilon_2]$ at constant height $z_0$ according to:

$$\text{LDOS}(x, y, z_0) = \sum_n |\psi_n(r)|^2 \text{ for all } n \text{ with } E_n \in [\varepsilon_1, \varepsilon_2]$$  \hspace{1cm} (3)

The results of the band-structure calculations for the 7-AGNR-S(1,3) and 7-AGNR-I(1,3) structures are compared to DFT calculations in Supplementary Fig. 12.

Molecular precursor and nanoribbon synthesis. The chemical synthesis of the monomers 1 (BADMT), 2 (BATMP) and 3 (DBBA) is detailed in the Supplementary Information together with details of the on-surface synthesis of the corresponding GNRs (Supplementary Scheme 1, Supplementary Figs. 28–38, 24–26).

STM/STS and nc-AFM characterization. A commercial low-temperature STM/AFM system (Scienta Omicron) with a base pressure below $1 \times 10^{-10} \text{ mbar}$ was used for sample preparation and characterization under ultrahigh-vacuum conditions. STM images and differential conductance $dI/dV$ maps were recorded in constant-current mode unless noted otherwise. Constant-height tunnelling current and nc-AFM frequency shift images were recorded with a CO-functionalized tip attached to a quartz tuning fork sensor (resonance frequency 23.5 kHz). $dI/dV$ spectra were recorded using the lock-in technique ($U_{\text{rms}} = 20 \text{ mV}$ at 680 Hz modulation). All data shown were acquired at a sample temperature of 5 K.

Data availability. The datasets generated and/or analysed during the current study are available from the corresponding author on reasonable request.

Code availability. The tight-binding calculations were performed using a custom-made code on the WaveMetrics IGOR Pro platform. Details of this tight-binding code can be obtained from the corresponding author on reasonable request.