The prospect of using graphene nanoribbons (GNRs) as next-generation nanoelectronic components has strengthened since their first bottom-up synthesis just over a decade ago (1, 2). Much excitement has been generated by their expected conductance properties as well as the tremendous control over nanoribbon geometry provided by chemical bottom-up methodologies and the resulting unparalleled tunability of their electronic structure. Early research largely focused on the potential role of GNRs in field-effect transistors (3, 4), revolving around tailoring the size of their bandgap through width, edge, and heteroatom engineering (2, 5–7), as well as the formation of heterojunctions through copolymerization (5, 8). Recently, the design of ever more intricate GNR structures has opened new avenues of exploration, including topics such as negative differential resistance (9–12), spintronics (13, 14), magnetism (15–20), and quantum information processing (21–23).

A common ingredient in many new GNR concepts is the controlled formation of low-energy modes and localized states. Methods to generate localized zero-energy modes include the generation of local sublattice imbalances, the linkage of GNR segments having different topological character (24–27), and the inclusion of heteroatoms in the GNR backbone (28–30). Recently, the incorporation of nonhexagonal rings into GNRs has also been presented as a method to fabricate new localized states (31–33). Four-membered rings are an exciting candidate for this type of application due to the strong antiaromatic character of cyclobutadienoid (CBD) groups (34–37). Nanoribbons with four-membered rings, however, have so far remained elusive due to challenges in their chemical synthesis (38). Although [2 + 2] cycloaddition has been shown to generate four-membered rings via on-surface synthesis, it has so far only been used to couple smaller acenes and triphenylenes (31, 39–42). The CBD units in these systems exhibit relatively little antiaromaticity due to their fusion pattern (i.e., because the CBD bonds have more single bond character in the dominant resonance structures that maximize the number of Clar sextets), resulting in a large bandgap (31, 36, 43). An exception is the formation of pyrene-type GNRs from a tetrabromopyrene precursor (38), but growth of this GNR was severely hampered by bromine atoms poisoning the catalytic activity of the gold surface and so only very short GNRs could be produced after actively removing halogens during synthesis through hydrogen dosing. Moreover, electronic characterization was not performed, and so the effect of CBD incorporation in those GNRs is so far unknown. More recently, a dehydrofluorination of fluoropolyphenylenes was used to make biphenylene networks exhibiting four-, six-, and eight-membered rings featuring a width-dependent electronic structure (44).

Here, we describe a strategy for fabricating linearly fused coronene-CBD GNRs (cor4GNR) through surface density–assisted coupling of tetrabromocoronene precursors. This GNR contains highly antiaromatic four-membered rings that greatly affect its electronic properties. We have performed simulations of the cor4GNR electronic structure based on density functional theory (DFT) that show how antiaromaticity of the CBD units translates into emergent low-energy electronic bands that would otherwise be absent in fully aromatic nanoribbons. Other characteristic properties include an indirect bandgap and dispersive band states composed of linear chains of p₅- and p₆-type pseudo-atomic orbitals localized on the CBDs. Synthesis of our cor4GNRs is implemented through direct contact transfer (DCT) of brominated coronene derivatives followed by thermally activated [2 + 2] cycloaddition. Coupling occurs exclusively in ultradense surface regions, showing that cyclodaddition of these molecules is possible without the need for dosed hydrogen in the presence of high surface coverage. The structure of the resulting GNRs was determined by bond-resolved scanning tunneling microscopy (BRSTM), which verified the expected geometry incorporating embedded CBDs. Electronic characterization of the GNRs was performed by scanning tunneling spectroscopy (STS) measurements as well as two-terminal transport through cor4GNRs.
RESULTS

Theoretical analysis of cor₄GNRs

We start by calculating the DFT electronic structure of a cor₄GNR containing pendant anhydride groups (1b) fused through CBDs as shown in Fig. 1A. The DFT-calculated electronic band dispersion is displayed in Fig. 1B, where the projection of the wave function onto the CBDs is indicated by the green shading of the bands. The ribbon exhibits a pair of bands at low energy with predominant localization on the CBDs. This is also evident in the total (gray) and local (green) densities of states (shown to the right), which reveal band onsets around $E = \pm 0.4 \, \text{eV}$ with high orbital density on the CBDs (resulting in an energy gap of $E_g = 0.8 \, \text{eV}$). The GNR orbitals shown in Fig. 1C support the picture of wave function localization at the CBD interfaces and reveal an additional notable feature: the CB states have a single nodal plane on the CBs aligned with the GNR axis (the $x$ direction), whereas the VB states have a nodal plane aligned perpendicular to it (the $y$ direction). The orbital patterns on the CBs are thus reminiscent of $p_x$ and $p_y$-type atomic orbitals with an out-of-plane angular momentum of $l = 1$. We therefore refer to them as $p_x$ and $p_y$ pseudo-atomic orbitals.

The emergence of electronic bands relatively close to the Fermi energy (especially considering the narrow size of these GNRs) is a consequence of the antiaromatic nature of the CBDs. This can be understood by considering the $\pi$-based frontier orbitals of the most fundamental molecular motifs from which the GNR is composed: hexagonal benzene and tetragonal cyclobutadiene. Figure 1D shows the results of DFT calculations of the orbitals of benzene and cyclobutadiene organized in constructs known as Frost circles, where energy increases along the vertical axis and the horizontal axis is associated with electron angular momentum ($l$). By counting the $\pi$-electrons, it can be seen that benzene is gapped, stable, and therefore aromatic at charge neutrality, whereas cyclobutadiene features a degenerate ground state and is thus antiaromatic: a result also known as Hückel’s rule. Because of its fourfold symmetry, cyclobutadiene can be interpreted as a pseudo-atom with frontier states that are $p_x$ and $p_y$ pseudo-atomic orbitals with an out-of-plane angular momentum of $l = 1$ (Fig. 1D). The bonding and antibonding states can similarly be interpreted as $s$- and $d_{xy}$-type orbitals. In regard to the GNR electronic structure, the $p_x$ and $p_y$ pseudo-atomic orbitals constitute a basis that dominates the low-energy band structure in an energetic region where the coronene subunits are themselves gapped. In the case of the cor₄GNR, one black band can be seen to intersect the $p_y$ band, but its wave function is predominantly localized on the anhydride side groups, meaning that the presence of this band is specific to this ribbon and not a general feature of CBD GNRs. Because the CBDs are organized in a linear chain (Fig. 1A), the $p_x$ and $p_y$ pseudo-atomic orbitals hybridize to give a typical linear-chain dispersion of the form $E = E_0 - 2t \cos(ka)$, where $t$ is the effective hopping strength between $p_x$ and $p_y$ basis.
states. Fitting this tight-binding model to the DFT-calculated \( p_x \) and \( p_y \) bands of Fig. 1 results in an inter-cyclobutadiene hopping parameter \( t \) of roughly 200 meV.

Another interesting feature seen in the cor\(_4\)GNR band structure is electron-hole “antisymmetry.” For every bonding state at \( E_b - E \) at momentum \( k \), there is, to good approximation, an antibonding state at \( E_b + E \) at momentum \( X - k \). Electron-hole symmetry is known to arise naturally from the chiral symmetry of graphene: Every bonding wave function has an antibonding partner at opposite energy relative to the Fermi level. However, the bipartite quality of cor\(_4\)GNRs requires a “sublattice unit cell” that is twice as large as the normal unit cell (Fig. 1A) because the four-membered rings swap the A and B sublattices on adjacent units. Hence, proper electron-hole symmetry in cor\(_4\)GNRs requires the band structure to be folded. This explains why the unfolded band structure (Fig. 1A) is antisymmetric in electron momentum. Electron-hole “antisymmetry” thus dictates that CBD GNRs will be indirect-gap semiconductors.

The emergence of \( p_x \) and \( p_y \) pseudo-atomic orbital GNR bands with indirect bandgaps is a general property of linked CBDs and is mostly independent of the specific molecular structure that lies between the four-membered rings. This is supported by additional DFT calculations that we performed on GNRs where the anhydride pendant groups were omitted, as well as GNRs where the coronene units were exchanged for pyrene and ovolene units, as shown in fig. S1. In each case, antisymmetric \( p_x \) and \( p_y \) bands emerge with effective dispersions of the form \( E = E_0 - 2f \cos(ka) \). The incorporation of CBD units into GNRs can thus be viewed as a general strategy for engineering GNRs that have a narrow indirect bandgap and that feature pairs of dispersive bands at low energy. The polyaromatic hydrocarbon spacer elements between the four-membered rings serve only to modulate the bandgap and bandwidth of the emergent \( p_x \) and \( p_y \) pseudo-atomic bands.

### Synthesis of cor\(_4\)GNRs

We now discuss the synthesis of cor\(_4\)GNRs, as shown schematically in Fig. 2A. The molecular precursor for the anhydride cor\(_4\)GNR (1a) is tetrabromocoronen di-anhydride 1a and was synthesized by saponification of alkylated coronene diimide 2a′ with potassium hydroxide, followed by dehydration in acetic acid [fig. S7; matrix-assisted laser desorption/ionization–time-of-flight (MALDI-TOF) data shown in fig. S8]. The prime in 2a′ denotes the alkylated molecule, to contrast it with the pure tetrabromocoronen diimide 2a, which was also used for experiments (synthesis and characterization of which are shown in figs. S9 and S10, respectively). We initially attempted to deposit precursor 1a onto Au(111) through sublimation from a Knudsen cell, but the precursor was unstable and pyrolyzed at elevated temperature before it could sublimate. We therefore turned to DCT to transfer precursor 1a onto the Au(111) surface, as shown schematically in Fig. 2B (where an applicator directly deposits its precursor powder onto the surface via mechanical contact) (48).

The DCT methodology leads to highly nonhomogeneous samples with molecular coverage ranging from the submonolayer regime to the multilayer regime depending on the distance from the point where the applicator contacts the surface. Gentle heating of the sample to \( T = 200^\circ\) C caused diffusion of the deposited molecules and resulted in large regions of the surface exhibiting full monolayer (ML) coverage.

Areas having 0.6 to 1.0 ML coverage exhibit rich self-assembly behavior as seen in Fig. 2 (C to E). The dominant van der Waals–bonded structure (type I) is shown in Fig. 2 (C and D) and exhibits fourfold rotational symmetry (\( C_{4v} \)) while remaining chiral because the molecular axes of the oblate precursor 1a are slanted off the axes of the two-dimensional (2D) crystal lattice [see fig. S2, which shows experimental details for the very similar coronene diimide (2a) for more structural details]. Another common morphology (type II) is shown in Fig. 2E and features compression of the molecules in the rows (compared to Fig. 2D) and separation of the molecules in the columns. Other less common self-assembly patterns are shown in fig. S3. Further heating of the sample to \( T = 270^\circ\) C causes a marked change in morphology as seen in Fig. 2F. Here, the molecules have covalently bonded into ribbon-like structures with 2 to 12 repeating
units. Other areas show highly ordered nanoribbon arrays, as shown in Fig. 2G. Conversion of the van der Waals–bonded self-assemblies of Fig. 2 (C to E) into the covalently bonded GNRs of Fig. 2 (F and G) was found almost exclusively in ultradense surface regions, while only sporadic GNR formation was found in areas with coverage between 0.9 and 1 ML (see fig. S4). Growth did not take place at all in areas with coverage below 0.9 ML, with these areas persistently featuring the van der Waals–bonded self-assemblies described above, despite the higher temperature anneal. In some very dense areas, covalently bonded GNRs “crowded” on top of each other, effectively creating GNR-intercalated GNRs (fig. S4). Upon heating further up to $T > 330^\circ$C, some coupling between monomers is observed in the lower-coverage areas, but the coupling becomes nondirectional and results in short, poor-quality graphitic structures, as shown in fig. S3. High surface density appears to play a critical role in the formation of covalently bonded cor$_4$GNRs.

**Structural analysis**

To verify that the GNR product from precursor 1a is the desired $[2 + 2]$ cycloaddition product and not an unwanted fusion product, we performed BRSTM measurements with a molecule-passivated tip (49). An STM topograph of a region with cor$_4$GNRs is shown in Fig. 3A, and a proposed structural model of the GNRs is shown in Fig. 3B. Figure 3C shows a BRSTM scan of the boxed region of Fig. 3A, which reproduces the carbon–carbon bonds of the proposed model. A close-up scan of a CBD linkage is shown in Fig. 3D, and the corresponding structural model can be seen in Figure 3E. The four-membered ring can be recognized in the center, although the bonds on the side are not well resolved due to a bowtie-like effect in the contrast. This effect is a consequence of the energetic proximity of band states near the Fermi level. The distorted six-membered rings seen at the sides of the GNR are similar to what has been observed before on related anhydride-containing molecules (50), although the large contrast seen here between different groups suggests an inhomogeneous interaction with the underlying gold substrate (51). The image distortions are tentatively ascribed to interaction of the molecule-passivated tip with the resulting inhomogeneous charge distribution (possibly involving radical formation). Regardless of the edge intricacies, the backbone of the GNR remains well resolved and the GNR can be assigned as a $[2 + 2]$ coupling product with CBDs.

**Electronic characterization**

We performed in-depth electronic structure measurements on the cor$_4$GNRs using STS. Figure 4A shows an STM image of an octameric cor$_4$GNR. The wave function distribution in this GNR was determined by mapping the differential conductance at constant height for both positive and negative bias voltages. The results, shown in Fig. 4B, reveal a chain of vertically aligned pairs of bright spots at the locations of the CBD units in the empty-state image ($V > 0$), and a chain of horizontally aligned bright spots at the locations of the CBD units in the filled-state image ($V < 0$). The empty-state $dI/dV$ map of the CBD units strongly resembles the $p_x$-band wave function shown in Fig. 1C, whereas the CBD filled-state map resembles the $p_y$-band wave function (rotated 90° relative to $p_x$). To confirm the identity of the experimentally measured GNR states, we calculated the theoretical local density of states (LDOS) of the cor$_4$GNR for both the empty-state $p_x$ band and the filled-state $p_y$ band (Fig. 4C). These theoretical LDOS maps match the experimental data in Fig. 4B, providing further evidence that we are experimentally observing the $p_x$ and $p_y$ pseudo-atomic orbitals expected to accompany CBD units in a cor$_4$GNR. The slight discrepancy between the experimental and theoretical LDOS patterns, e.g., the two-lobe pattern instead of the three-lobe pattern on the sides of the coronene subunits,
emphasize $p_x$-band states (red) and $p_y$-band states (teal) (the spectroscopy positions are marked in the topograph of Fig. 4A). Both spectra show a reasonably clear VB onset at $V = -0.6$ V, but only the blue spectrum shows a conduction band onset near $V = 0.1$ V. Both spectra show higher energy upturns in $dI/dV$ (i.e., $V = -1.8$ V and $V = 1.6$ V) that likely mark the onset of higher energy bands.

The results of in situ lifting experiments can be seen in Fig. 4E. This technique is useful for gaining insight into the two-terminal transport properties of GNRs, as well as the intrinsic GNR electronic structure in the absence of a substrate (10, 52). Figure 3A shows the ribbon that was lifted by attaching the tip to the side of the last unit of the GNR (marked by a red cross in the figure). Figure 4E shows the two-point transport differential conductance as a function of voltage for low tip heights in the range $1 \text{ nm} < z < 2.2 \text{ nm}$ (gray spectra) and for near detachment at $z = 7 \text{ nm}$ (blue spectrum). As the GNR is lifted, the states in the energy gap region ($-0.6 \text{ V} < V < 0.1 \text{ V}$) are swept away, implying that they arise mainly from tunneling into the Au(111) surface (consistent with the STS of Fig. 4D). The most prominent feature that remains is a peak at $V \approx -0.6$ V, which marks the VB onset. The amplitude of this feature decays as $G = G_0 e^{-\beta z}$ with a decay parameter $\beta = 2.7 \text{ nm}^{-1}$, signaling off-resonant transport (10, 52, 53). When the ribbon is pulled away from the surface to a height of 7 nm, the VB fingerprint disappears entirely and the CB conductance also decays notably, leaving onsets at $V = -1.5 \text{ V}$ and $V = 0.8 \text{ V}$. The off-resonant character of the transport through the $p_x$- and $p_y$-type states can be understood from their localized nature. When lifted, the initial particle-in-a-box states inside the $p_x$ and $p_y$ bands no longer constitute ballistic transport channels between tip and surface because the individual CBD units may be separated electrostatically, causing the transport to attain a more hopping-like character. At large tip heights, the only remaining transport channels are formed by fully delocalized states that connect well to both tip and surface: states from the black bands of the electron dispersion of Fig. 1B. The experimentally observed exponential decay (with $z$) of the VB feature thus provides additional evidence that it arises from CBD-derived $p_x$-band states.

**DISCUSSION**

These results can be thought of as “inverting” the normal GNR paradigm, where functionality is designed into precursor molecules that become the unit cells for quasi-1D GNR crystals where intercell linkages are of secondary importance. In cor4GNRs, it is the linkages between precursor units that are paramount, while the precursor itself has only a secondary influence on the band structure that emerges from the coupling between linkage groups. Our STS results support this picture and demonstrate that four-membered GNR linkages host frontier states that lead to dispersive bands composed of $p_x$ and $p_y$ pseudoatomic orbitals. Other than providing coupling between CBDs, the precursor structure mainly just determines the dielectric environment of the CBD-derived $p_x$ and $p_y$ bands. Two-terminal transport reveals fingerprints of these CBD band states through the decay of the signal at increased tip height. The narrow energy gap of cor4GNRs as well as the bandgap’s indirect nature and the dispersive character of the frontier bands are all consequences of the CBD lattice and are not specific to any coronene backbone or pendant groups.

The cor4GNR properties described here should be generalizable to other CBD GNRs, as corroborated by our DFT calculations on
The pseudo-atomic orbital physics of such GNRs could potentially be exploited in new designer quantum systems, an example of which might be the placement of alternating molecular segments between CBD units (shown in fig. S6) to experimentally realize new effective Su-Schrieffer-Heeger models (27, 47, 54–56).

MATERIALS AND METHODS

Synthesis

1a was prepared from 2a' (see fig. S7) according to the following procedure: To a 20-ml vial was added 2a' (20 mg, 0.19 mmol), potassium hydroxide (50 mg, 0.89 mmol), tert-butyl alcohol (4 ml), and a magnetic stirring bar. The vial was sealed with a Teflon cap and stirred at T = 90°C for 4 hours. Acetic acid (7 ml) was then added to the reaction mixture, and the mixture was stirred at T = 70°C for 2 hours. The solid was then filtered and washed with H2O, dichloromethane, and acetone to get 1a as an orange solid (11 mg, 80% yield). Synthesis of 2a and 2a', as well as MALDI-TOF characterization of 1a and 2a, is shown in figs. S7 to S10.

Sample preparation

Atomically clean Au(111) surfaces were prepared through repeated cycles of argon ion (Ar+) bombardment and annealing. Tetrabromocorone-dianhydride (1a) was introduced onto the surface through DCT using the same setup as described in our previous work (57). The glass fiber was cleaned using various solvents and subsequently oven-dried at T = 50°C (93°C for 500°C) for 2 hours. The solid was then filtered and washed with H2O, dichloromethane, and acetone to get 1a as an orange solid (11 mg, 80% yield). Tetrabromocorone-dianhydride (1a) was introduced onto the surface through DCT using the same setup as described in our previous work (57).

STM measurements

All STM experiments were carried out using a commercial Createc LT-STM held at T = 4.5 K using platinum-iridium tips. Image processing of the STM scans was performed using WSxM software (58). S. STS and differential conductance mapping experiments were performed with the use of a lock-in amplifier using a wiggle voltage amplitude (Vac) of 4 to 20 mV at a frequency (f) of 620 Hz or 577.7 Hz. Transport experiments were performed according to the procedure described in (10). BRSTM measurements were performed by passivating the tip with a molecule from the surface, followed by imaging the current at constant height and low bias. Differential conductance mapping was also performed using a passivated tip. In both cases, the atomic or molecular species passivating the tip is unknown and difficult to control as the full coverage of the samples prohibits the controlled pickup of any identifiable molecule. Passivation was therefore achieved at random by poking the tip around the edges of the GNRs.

Calculations

Periodic DFT calculations were carried out using the Quantum ESPRESSO package (59). All structures were fully relaxed until all force components were smaller than 0.01 eV Å⁻¹. We used 60 Ry as the plane-wave cutoff and Perdew-Burke-Ernzerhof (PBE) norm-conserving pseudopotentials. A vacuum region of 15 Å was added in the nonperiodic direction to prevent interactions between replicas. Finite DFT calculations (Fig. 1E) were performed using ORCA (60). The geometry was optimized until all force components were smaller than 2.6 10⁻⁸ eV Å⁻¹. The def2-SV(P) basis set was selected together with the B3LYP exchange-correlation functional. Molecular and crystal orbitals were rendered using MathemaTB (61).

Supplementary materials

Supplementary material for this article is available at https://science.org/doi/10.1126/sciadv.abf8592

References and notes

1. J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Mooto, A. P. Seitsonen, M. Saleh, X. Feng, K. Muller, R. Fasel, Atomically precise bottom-up fabrication of graphene nanoribbons. Nature 466, 470–473 (2010).
2. L. Talirz, P. Ruffieux, R. Fasel, On-surface synthesis of atomically precise graphene nanoribbons. Adv. Mater. 28, 6222–6231 (2016).
3. F. Schwierz, Graphene transistors. Nat. Nanotechnol. 5, 487–496 (2010).
4. P. B. Bennett, Z. Pedramrazi, A. Madani, Y.-C. Chen, D. G. de Oteyza, C. Chen, F. R. Fischer, M. F. Crommie, J. Bokor, Bottom-up graphene nanoribbon field-effect transistors. Appl. Phys. Lett. 103, 253114 (2013).
5. C. Bronner, S. Stremnall, M. Gille, F. Braufle, A. Haase, S. Hecht, P. Tegeder, Aligning the band gap of graphene nanoribbons by monomer doping. Angew. Chemie Int. Ed. 52, 4422–4425 (2013).
6. N. Merino-Diez, A. Garcia-Lekue, E. Carbonell-Sanzombli, J. Li, M. Corso, L. Colalozzo, F. Sedona, D. Sanchez-Portail, J. P. Pascual, D. G. De Oteyza, Width-dependent band gap in armchair graphene nanoribbons reveals fermi level pinning on Au(111). ACS Nano 11, 11661–11668 (2017).
7. R. S. K. Houtsma, J. de la Rie, M. Stohr, Atomically precise graphene nanoribbons: Interplay of structural and electronic properties. Chem. Soc. Rev. 50, 6541–6568 (2011).
8. J. Cai, C. A. Pignedoli, L. Talirz, P. Ruffieux, H. Söde, L. Liang, V. Meunier, R. Berger, R. Li, X. Feng, K. Muller, R. Fasel, Graphene nanoribbon heterojunctions. Nat. Nanotechnol. 9, 896–900 (2014).
9. S. Smith, J.-P. Linhas, J. Bokor, S. Salahuddin, Negative differential resistance and steep switching in chevron graphene nanoribbon field-effect transistors. IEEE Electron Device Lett. 39, 143–146 (2018).
10. P. H. Jacobse, A. Kimouche, T. Gebraad, M. M. Ervasti, J. M. Thijssen, P. Liljeroth, I. Swart, Electronic components embedded in a single graphene nanoribbon. Nat. Commun. 8, 119 (2017).
11. D. Nozaki, Lokamani, A. Santana-Bonilla, A. Dianat, R. Gutierrez, C. Cuniberti, Switchable negative differential resistance induced by quantum interference effects in porphyrin-based molecular junctions. J. Phys. Chem. Lett. 6, 3950–3955 (2015).
12. H. Ren, Q.-X. Li, Y. Luo, J. Yang, Graphene nanoribbon as a negative differential resistance device. Appl. Phys. Lett. 94, 173110 (2009).
13. P. Ruffieux, S. Wang, B. Yang, C. Sanchez-Sanchez, J. Liu, T. Dielen, L. Talirz, P. Shindne, C. A. Pignedoli, D. Passerone, T. Dumsafl, X. Feng, K. Muller, R. Fasel, On-surface synthesis of graphene nanoribbons with zigzag edge topology. Nature 531, 489–492 (2016).
14. X. Kong, B. Cui, W. Zhao, J. Zhao, D. Li, D. Liu, Spin negative differential resistance and high spin filtering behavior realized by devices based on graphene nanoribbons and graphitic carbon nitrides. Org. Electron. 15, 3674–3680 (2014).
15. O. V. Yazyev, Emergence of magnetism in graphene materials and nanostructures. Rep. Prog. Phys. 73, 56501 (2010).
16. S. Mishra, D. Beyer, K. Emme, S. Kezliebkeie, R. Berger, D. Gröning, C. A. Pignedoli, K. Muller, P. Liljeroth, P. Ruffieux, X. Feng, R. Fasel, Topological frustration induces unconventional magnetism in a nanographene. Nat. Nanotechnol. 15, 22–28 (2020).
17. J. Li, S. Sanz, M. Corso, D. J. Choi, D. Peña, T. Frederiksen, J. I. Pascual, Single spin localization and manipulation in graphene open-shell nanostructures. Nat. Commun. 10, 200 (2019).
18. M. Slota, A. Keerthi, W. K. Myers, E. Tretyakov, M. Baumgarten, A. Ardavan, H. Sadeghi, C. J. Lambert, A. Narita, K. Muller, L. Bogani, Magnetic edge states and coherent manipulation of graphene nanoribbons. Nat. Communications 557, 691–695 (2018).
19. Y. Zheng, C. Li, C. Xu, D. Beyer, X. Yue, Y. Zhao, G. Wang, D. Guan, Y. Li, H. Zheng, C. Liu, J. Liu, X. Wang, W. Luo, X. Feng, S. Wang, J. Jia, Designer spin order in diradical nanographenes. Nat. Commun. 11, 6076 (2020).
20. S. Song, J. Su, M. Telychko, J. Li, G. Li, Y. Li, C. Su, J. Wu, J. Liu, On-surface synthesis of graphene nanoribbons with n-magnetism. Chem. Soc. Rev. 50, 3238–3262 (2021).
21. C.-C. Chen, Y.-C. Chang, Theoretical studies of graphene nanoribbon quantum dot qubits. Phys. Rev. B 92, 245406 (2015).
23. G.-P. Guo, Z.-R. Lin, X.-P. Li, T. Tu, G. Cao, G.-C. Guo, Quantum computation with graphene nanoribbons, New J. Phys. 11, 123005 (2009).
24. T. Cao, F. Zhao, S. G. Louie, Topological phases in graphene nanoribbons: Junction states, spin centers, and quantum spin chains. Phys. Rev. Lett. 119, 076401 (2017).
25. Y. L. Lee, F. Zhao, T. Cao, J. Ihm, S. G. Louie, Topological phases in cove- edged and chevron graphene nanoribbons: Geometric structures, Z 2 invariants, and junction states. Nanoph. Lett. 18, 7247–7253 (2018).
26. D. J. Rizzo, G. Veber, T. Cao, C. Bronner, T. Chen, F. Zhao, H. Rodriguez, S. G. Louie, M. F. Crommie, F. R. Fischer, Topological band engineering of graphene nanoribbons. Nature 560, 204–208 (2018).
27. O. Gröning, S. Wang, X. Yao, C. A. Pignedelli, G. Borin Barin, C. Daniels, A. Cupo, V. Meunier, X. Feng, A. Narita, K. Mullern, P. Ruffieux, R. Fasel, Engineering of robust topological quantum phases in graphene nanoribbons. Nature 560, 209–213 (2018).
28. R. R. Cloke, T. Marangoni, G. D. Nguyen, T. Joshi, D. J. Rizzo, C. Bronner, T. Cao, S. G. Louie, M. F. Crommie, F. R. Fischer, Site-specific substitutional boron doping of semiconducting armchair graphene nanoribbons. J. Am. Chem. Soc. 137, 8872–8875 (2015).
29. S. Kawai, S. Satoh, S. Osumi, S. Yamaguchi, A. S. Foster, P. Spierig, E. Meyer, Atomically controlled substitutional boron-doping of graphene nanoribbons. Nat. Commun. 6, 8098 (2015).
30. S. Kawai, Nakatsuka, T. Hatakeyama, R. Pawlik, T. Meier, J. Tracey, E. Meyer, A. S. Foster, Multiple heteroatom substitution to graphene nanoribbons. Sci. Adv. 4, eaar7118 (2018).
31. C. Sánchez-Sánchez, T. Diener, A. Nicolai, N. Kharche, L. Liang, C. Daniels, V. Meunier, J. Liu, X. Feng, K. Mullern, J. R. Sánchez-Valencia, O. Gröning, P. Ruffieux, R. Fasel, On-surface synthesis and characterization of acene-based nanoribbons incorporating four-membered rings. Chem. A Eur. J. 25, 12074–12082 (2019).
32. M. Liu, M. Liu, L. Shi, Z. Zhu, J. Pan, S. Li, T. Li, Y. He, Z. Cai, J. Wang, Y. Zheng, X. Qiu, D. Zhong, Graphene-like nanoribbons periodically embedded with four- and eight-membered rings. Nat. Commun. 8, 14924 (2017).
33. P. H. Jacobse, R. D. McCurdy, J. Jiang, D. J. Rizzo, G. Veber, P. Butler, R. Zuzak, S. G. Louie, F. R. Fischer, M. F. Crommie, Bottom-up assembly of nanoribbons graphene with emergent electronic states. J. Am. Chem. Soc. 142, 13507–13514 (2020).
34. Y. C. Teo, Z. Jin, Y. Xian, Synthesis of cyclobutadienoid-fused phenazines with strongly repulsion in scanning tunneling microscopy. Phys. Rev. Lett. 105, 86103 (2010).
35. P. Cui, Q. Zhang, H. Zhu, X. Li, W. Wang, Q. Li, C. Zeng, Z. Zhang, Carbon tetragons as definitive spin switches in narrow zigzag graphene nanoribbons. Phys. Rev. Lett. 116, 266802 (2016).
36. Z. Jin, Y. C. Teo, S. J. Teat, Y. Xian, Regioselective synthesis of [3]napthylene and tuning spin centers, and quantum spin chains. Phys. Rev. Lett. 119, 11009 (2019).
37. O. Š. Miljanić, K. P. C. Vollhardt, [N]Phenylenes: A novel class of cyclohexatrienoid molecules. J. Am. Chem. Soc. 135, 8872–8875 (2013).
38. M. S. G. Mohammed, J. Lawrence, F. García, P. Brandimarte, A. Berdonces-Layunta, R. Zhang, B. Xia, H. Xu, N. Lin, Kinetically controlled synthesis of four- and six-membered rings. Nat. Commun. 6, 24802 (2015).
39. M. N. Huda, S. Kezeliebieke, P. Lijjorhet, Designer flat bands in quasi-one-dimensional atomic lattices. Phys. Rev. Res. 2, 043246 (2020).
40. R. Drost, T. Ojansj, A. Harju, P. Lijjorhet, Topological states in engineered atomic lattices. Nat. Phys. 13, 668–671 (2017).
41. L. Yan, P. Lijjorhet, Engineered electronic states in atomically precise artificial lattices and graphene nanoribbons. Adv. Phys. X. 4, 1651672 (2019).
42. R. D. McCurdy, P. H. Jacobsse, I. Piskun, G. C. Veber, D. J. Rizzo, R. Zuzak, Z. Mutlu, J. Bokor, M. F. Crommie, F. R. Fischer, Synergetic bottom-up synthesis of graphene nanoribbons by matrix-assisted direct transfer. J. Am. Chem. Soc. 143, 4174–4178 (2021).
43. J. Horcaj, R. Fernández J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrera, A. M. Baro, WSXM: A software for scanning probe microscopy and a tool for nanotechnology. Rev. Sci. Instrum. 78, 013705 (2007).
44. P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, D. A. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Stracca, S. Scandolo, G. Scuseria, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch, QUANTUM ESPRESSO: A modular and open-source software package for quantum simulations of materials. J. Phys. Condens. Matter. 21, 395002 (2009).
45. F. Neese, F. Wemmnoks, U. Becker, C. Riplinger, The ORCA quantum chemistry program package. J. Chem. Phys. 152, 232104 (2020).
46. P. H. Jacobsse, MathemaTB: A Mathematica package for tight-binding calculations. Comput. Phys. Commun. 244, 392–408 (2019).
47. T. Liu, Y. Ge, B. Sun, B. Fowler, H. Li, C. Nuckolls, S. Xian, Synthesis, regioselective bromination, and functionalization of coronene tetracarboxydiimide. J. Org. Chem. 84, 2713–2720 (2019).

Acknowledgments
Funding: This research was supported by the Office of Naval Research MURI Program N00014-16-1-2921 (molecular design, STM spectroscopy, and band structure); by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under the Nanomachine Program award number DE-AC02-05CH11231 (molecular self-assembly, image analysis, and structural relaxation studies); by the NSF under grants DMR-1926004 (LSDA simulations) and DMR-1839098 (-p band analysis); and by the Frontera Computing Project at the Texas Advanced Computing Center, under award number OAC-1818253 (surface interactions). Computational resources were provided by the DOE Lawrence Berkeley National Laboratory HPC/NSERC facility and by the NSF through XSEDE resources at NICS. P.H.J. acknowledges fellowship support from the Dutch Research Council through the Rubicon Award (019.1828.18). C.N. thanks Sheldon and Dorothea Buckler for their generous support. Author contributions: Conceptualization: S.P., Z.J., C.N., and M.F.C. Chemical synthesis: S.P. and Z.J. STM investigation: P.H.J., Z.W., and D.J.R. Theoretical concepts: P.H.J. DFT calculations: J.J. and S.G.L. Supervision: S.G.L., C.N., and M.F.C. Writing—original draft: P.H.J. Writing—review and editing: all authors.

The authors declare that they have no competing interests.
Pseudo-atomic orbital behavior in graphene nanoribbons with four-membered rings

Peter H. JacobseZexin JinJingwei JiangSamuel PeurifoyZiqin YueZiyi WangDaniel J. RizzoSteven G. LouieColin NuckollsMichael F. Crommie

Sci. Adv., 7 (52), eabl5892. • DOI: 10.1126/sciadv.abl5892

View the article online
https://www.science.org/doi/10.1126/sciadv.abl5892
Permissions
https://www.science.org/help/reprints-and-permissions

Use of this article is subject to the Terms of service

Science Advances (ISSN ) is published by the American Association for the Advancement of Science. 1200 New York Avenue NW, Washington, DC 20005. The title Science Advances is a registered trademark of AAAS. Copyright © 2021 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution License 4.0 (CC BY).