Conjugated ladder polymers (CLPs) represent an attractive type of π-conjugated polymers which consist of a sequence of fused rings with adjacent rings sharing two or more atoms. The restriction of bond rotations inherent to CLPs represent an important approach that has been systematically pursued since the 1990s. Such rigidification generally provides enhanced intermolecular π–π stacking interactions and high thermal stability, which may lead to application-relevant properties (or improved materials properties), with prospects in organic field-effect transistors, organic light emitting diodes, gas separation or optically pumped lasers. While the majority of CLPs reported to date have been obtained through solution chemistry, the potential of on-surface synthesis to overcome some of the intrinsic challenges of solution-based approaches, including low solubility, high reactivity of reaction products or precursors and limited diversity of reaction designs, toward the effective fabrication of tailored ladder polymers has increasingly come to forth in the last decade.

In this context, graphene nanoribbons (GNRs) represent the most acknowledged class of CLPs. Despite the recent expansion of the GNR catalogue, the controlled incorporation of nonbenzenoid rings into the GNR backbone to modulate the structural and electronic properties remains comparatively scarce. Theoretical calculations have anticipated the existence of several nonbenzenoid carbon allotropes which are expected to exhibit pronouncedly different (opto)-electronic properties. Nevertheless, systematic investigations of the structural and electronic properties resulting from selective incorporation of nonbenzenoid rings into CLPs are still lacking.

In this work, we introduce an exemplary approach toward the on-surface formation of nonbenzenoid π-conjugated ladder-type polymers on a coinage metal surface under ultrahigh vacuum (UHV) conditions. To this end, we synthesized in solution 2,7-dibromocyclopenta[h]aceanthrylene as a precursor (1), which features electron acceptor properties due to the presence of the 5-membered rings. Compound 1 can be sublimed intact and converted to nonbenzenoid CLPs (3) by thermal activation on the metal surface (see ESI† for the precursor synthesis and characterization). The reaction route toward the formation of the CLP 3, illustrated in Scheme 1, follows two surface-assisted steps including dehalogenative homocoupling to yield an intermediate one-dimensional (1D) polymer (2) and cyclodehydrogenation to form 3. Interestingly, two different carbon–carbon (C–C) bonds between adjacent
monomers can be formed in the cyclodehydrogenation step, resulting in six- or five-membered ring formation between monomers (3a and 3b, respectively). All the synthesis steps are investigated by scanning tunneling microscopy (STM) and complemented by density-functional theory (DFT).

The chemical structure of 2 and 3 are unambiguously identified by ultrahigh-resolution STM (UHR-STM) and their electronic properties studied by scanning tunneling spectroscopy (STS).

To study the on-surface reactions illustrated in Scheme 1, we sublimed precursor 1 onto an atomically clean Au(111) surface held at room temperature and subsequently annealed at 330 °C. High-resolution STM images (Fig. 1a and b) reveal the predominant presence of 1D polymers together with rounded protrusions between the chains, which we assign to bromine atoms detached from 1. To confirm the chemical structure of 2, ultrahigh-resolution STM (UHR-STM) images acquired with a CO-functionalized tip recorded in the Pauli repulsion regime were performed (Fig. 1c). Hereby, intramolecular features corresponding to the cyclopenta[h]aceanthrylene molecular backbone linked via C–C bonds through the pentagons of each molecular subunit are distinguished (see Fig. S1† for a detailed STS and voltage dependent conductance spectra characterization of a segment of 2). Additionally, UHR-STM images allow us to discern single (s)-trans and (s)-cis isomers within the same polymer chain (see Scheme S1† for the reaction pathway between adjacent (s)-trans and (s)-cis isomers). The DFT-optimized equilibrium geometry of 2 shown in Fig. 1d indicates that the polymer adopts a planar configuration, with an adsorption height of 3.3 Å with respect to the underlying gold surface.

Annealing the sample at 400 °C induced minor variations in the molecular structure of 2 and only small segments of the 1D polymer (~8%), attributed to the onset of the cyclodehydrogenation reaction, present a different appearance (see Fig. S2† for STM and UHR-STM images). Only after a further annealing step at 420 °C, the formation of the targeted CLP 3, coexisting with a few laterally fused segments, is achieved (Fig. 2a). A zoom-in STM image (Fig. 2b), allows us to discern two different C–C coupling motifs in the formation of 3. Herein, the kinked linear segments observed in Fig. 2b are attributed to the formation of a hexagon/pentagon (3a/3b) between two molecular units (Fig. 2c and d). Importantly, statistics over the

![Scheme 1 On-surface synthesis of nonbenzenoid CLPs 3a and 3b.](image)

![Fig. 1 On-surface synthesis of the 1D polymer (2) on Au(111). (a) Overview STM topography image of the surface after deposition of 1 and subsequent annealing at 330 °C, showing the predominant presence of 1D chains. V_b = −0.50 V, I_t = 60 pA, scale bar: 10 nm. (b) High-resolution STM image of (a) where 1D chains together with rounded protrusions, assigned to bromine atoms, are observed. V_b = −0.20 V, I_t = 70 pA, scale bar: 2 nm. (c) CO-functionalized UHR-STM image of 2 where the intramolecular features of the nonbenzenoid molecular backbone in the polymers are discerned. s-cis and s-trans denote the two isomers found within a chain. V_b = 5 mV, I_t = 70 pA, scale bar: 2 nm. (d) Top view of the DFT equilibrium geometry of 2 on Au(111).](image)
coupling motifs observed for more than 500 molecular units indicates that the coupling through the six-membered ring is favoured over the five-membered one (3a = 58%, 3b = 32%, non-cyclodehydrogenated = 10%). This can be rationalized on the basis of simple energetic considerations. On the one hand, gas phase calculations for 3a and 3b reveal that 3a is ≈ 1 eV more energetically favoured compared to 3b. This energy difference is further enhanced on the substrate and 3a (Fig. 2f) is ≈ 1.7 eV more stable compared to 3b on Au(111). Configurations of the polymer units that would lead to the formation of 3b motifs are hindered by the fact that the polymer should undergo a torsion (deviating from linearity) that is unlikely to occur for long strands. Therefore, cyclodehydrogenation between adjacent s-trans/s-cis and s-cis/s-trans isomers (synthetic pathway (a) in Scheme S1) implies the formation of a new hexagon (3a), while cyclodehydrogenation between adjacent s-trans/s-trans and s-cis/s-cis isomers (synthetic pathway (b) in Scheme 1) affords the formation of a new pentagon (3b, with 3bI, 3bII ≈ 50%). In addition, it is expected that the reaction mechanisms in the formation of 3a and 3b involve a rotation of cyclopenta[4i]aceanthrylene molecular units on the surface substrate, at temperatures typical for the annealing, prior to cyclization (see synthetic pathway (a) in Scheme 1 and synthetic pathway (b) in Scheme S1).

Finally, Fig. 2e and f display the DFT equilibrium geometry of the formed pentagon (in green in Fig. 2e) and hexagon (in blue in Fig. 2f), respectively. Both adopt a planar configuration, with an adsorption height of 3.2 Å with respect to the underlying surface.

Next, we performed STS measurements on a 3a segment (six consecutive units), whose formation is favoured over 3b, to probe its electronic structure. Voltage-dependent differential conductance spectra (dI/dV vs. V) feature characteristic peaks at −1.12 eV and +0.65 eV (Fig. 3a), which are assigned to the valence band maximum (VBM) and the conduction band maximum (CBM), respectively, corresponding to an electronic structure of the polymer on Au(111). (a) Overview STM topography image of the surface after annealing 3 at 420 °C, showing the formation of fully conjugated nonbenzenoid CLPs. V0 = −0.10 V, I0 = 100 pA, scale bar: 5 nm. (b) High-resolution STM image of 3 where kinked and linear segments can be distinguished. V0 = 0.02 V, I0 = 100 pA, scale bar: 1 nm. (c and d) CO-functionalized UHR-STM image and corresponding chemical sketch of the segment of 3 shown in (b) where the intramolecular features, attributed to the formation of a six-membered (3a) and a five-membered (3b) ring, respectively, are discerned. V0 = 5 mV, I0 = 100 pA, scale bar: 1 nm. (e and f) Top views of the DFT equilibrium geometry of 3b and 3a respectively, on Au(111). Bonds and atoms highlighted in green and blue colours show the pentagon and hexagon formed due to the cyclodehydrogenation reaction.

**Fig. 2** On-surface synthesis of 3 on Au(111). (a) Overview STM topography image of the surface after annealing 3 at 420 °C, showing the formation of fully conjugated nonbenzenoid CLPs. V0 = −0.10 V, I0 = 100 pA, scale bar: 5 nm. (b) High-resolution STM image of 3 where kinked and linear segments can be distinguished. V0 = 0.02 V, I0 = 100 pA, scale bar: 1 nm. (c and d) CO-functionalized UHR-STM image and corresponding chemical sketch of the segment of 3 shown in (b) where the intramolecular features, attributed to the formation of a six-membered (3a) and a five-membered (3b) ring, respectively, are discerned. V0 = 5 mV, I0 = 100 pA, scale bar: 1 nm. (e and f) Top views of the DFT equilibrium geometry of 3b and 3a respectively, on Au(111). Bonds and atoms highlighted in green and blue colours show the pentagon and hexagon formed due to the cyclodehydrogenation reaction.

**Fig. 3** Electronic properties of 3a on Au(111). (a) dI/dV spectrum of 3a, acquired at the position indicated by the blue cross (blue line), revealing a band gap of 1.77 eV, and reference spectrum taken on the bare Au(111) surface (pink line). (b) DFT calculated band structure of an infinite CLP 3a in gas phase. (c and d) Constant-current differential conductance (dI/dV) maps (c) and corresponding DFT-calculated LDOS maps (d) at the energetic positions corresponding to the VB (top) and the CB (bottom) of 3a, respectively. Tunneling parameters for the dI/dV maps: VB (V0 = −1.10 V, I0 = 300 pA); CB (V0 = 0.70 V, I0 = 300 pA). All scale bars: 0.5 nm.
bandgap of 1.77 eV on Au(111), matching very well with the calculated band structure for an infinite 3a segment (Fig. 3b). Constant-current maps of the dl/dV signal of a 3a acquired with a CO-functionalized tip at the VBM (top) and CBM (bottom) energetic positions are shown in Fig. 3c (see Fig. S3 and S4† for comparison with the constant-height dl/dV maps of 3a as well as dl/dV vs. V and constant-current dl/dV maps of the minority 3b segment, respectively). Finally, the experimental dl/dV maps are well reproduced by the DFT-calculated local density of states (LDOS) maps for the CBM and VBM (Fig. 3d), calculated at 3 Å above the molecular plane.

In conclusion, we have demonstrated a novel synthetic pathway toward the on-surface fabrication of nonbenzenoid π-conjugated ladder-type polymers on Au(111) by a combination of high-resolution STM and STS complemented with DFT calculations. A first annealing step at 330 °C induces debrumination, leading to the formation of 1D polymers (2). A subsequent annealing step at 420 °C promotes the cyclodehydrogenation and the consequent formation of nonbenzenoid CLPs (3). Interestingly, two types of C–C coupling motifs, comprising the formation of a hexagon (3a) or a pentagon (3b) between cyclopenta[h]aceneanthylene subunits, are observed. Such C–C couplings arises from the presence of s-trans and s-cis isomers at the polymer step, though the formation of a hexagon, which implies cyclodehydrogenation between adjacent s-trans/s-cis and s-cis/s-trans isomers, is favoured over the formation of the pentagon (cyclodehydrogenation between adjacent s-trans/s-trans and s-cis/s-cis isomers). We expect that the synthetic strategy presented in this work is of general relevance for the synthesis of novel conjugated ladder-type polymers, and will contribute to expand the knowledge in this field with notable potential for device applications.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements

This work was supported by the Swiss National Science Foundation (200020_182015), the European Union’s Horizon 2020 research and innovation programme (GrapheneCore2 785219), the Office of Naval Research (N00014-18-1-2708), and the Swiss National Centre for Computational Design and Discovery of Novel Materials (MARVEL). The Swiss National Supercomputing Centre (CSCS) under project ID s904 is acknowledged for computational resources. M.K. gratefully acknowledges the generous funding by the Deutsche Forschungsgemeinschaft (DFG) – Project number 182849149 – SFB 953 “Synthetic Carbon Allotropes”.

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