Graphene-like nanoribbons periodically embedded with four- and eight-membered rings

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Graphene nanoribbons, defined as nanometer-wide strips of graphene, have attracted extensive attention as promising building blocks for nanoelectronics and spintronics. The electronic properties of nanoribbons can be modulated at nanoscale by controlling the edge structure and width [1], chemical doping [2] and formation of heterojunctions. Embedding non-hexagonal rings is considered a promising strategy to tailor the electronic properties of carbon-based nanomaterials. However, non-hexagonal rings are energetically unstable compared to the hexagonal counterparts, making it challenging to embed non-hexagonal rings in a controllable manner. Here, we report an on-surface synthesis of graphene-like nanoribbons with periodically embedded four- and eight-membered rings. The scanning tunnelling microscopy and atomic force microscopy study revealed that four- and eight-membered rings are formed between adjacent perylene backbones with a planar configuration. The nonhexagonal rings as a topological modification markedly change the electronic properties of the nanoribbons. The highest occupied and lowest unoccupied ribbon states are mainly distributed around the eight- and four-membered rings, respectively. The realization of graphene-like nanoribbons comprising non-hexagonal rings demonstrates a controllable route to fabricate non-hexagonal rings in nanoribbons and makes it possible to unveil their unique properties induced by non-hexagonal rings.

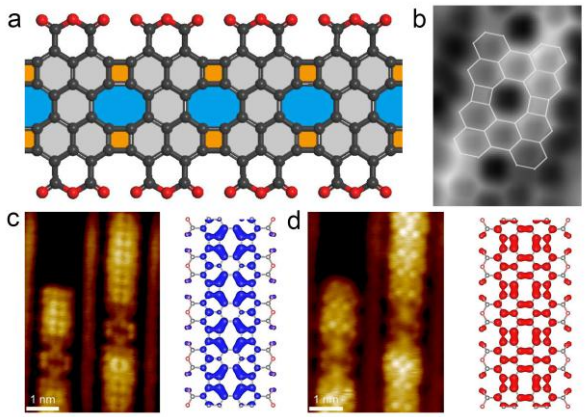

Figure 1 **a**, Schematic of graphene-like nanoribbon embedded with four- and eight-membered rings; **b**, Constant-height nc-AFM image with partly overlaid ribbon structure; **c**,**d** High-resolution STM images of graphene-like nanoribbons with PPP polymers on Au(111) obtained at V = –0.8 V (HO ribbon state) and V = 0.8 V (LU ribbon state) respectively (I = 0.6 nA).

[1] Ruffieux, P. *et al*. On-surface synthesis of graphene nanoribbons with zigzag edge topology. *Nature* **531**, 489–492 (2016).
[2] Kawai, S. *et al*. Atomically controlled substitutional boron-doping of graphene nanoribbons. *Nat. Commun.* **6**, 8098 (2015).

Suplementary information:

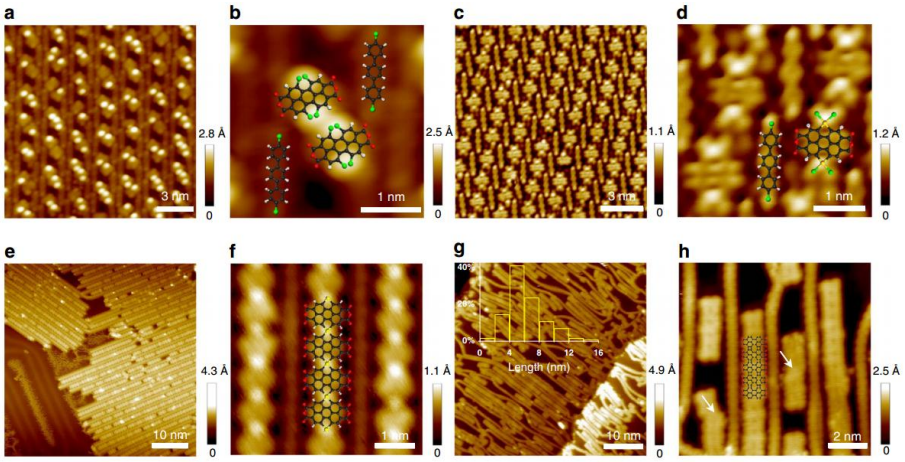

Figure 2 | Synthesis and characterization of graphene-like nanoribbons. a,**b** STM image of DBTP and Br_4-PTCDA molecules codeposited on Au(111) at RT (V = –2 V, I = 2.2 nA). **c**, STM image of the self-assembled structures of PTCDA-Au_2-Br_4 hybrids and DBTP molecules on Au (111) prepared at 100 °C (V = –0.1 V, I = 2 nA). **d**, High-resolution STM image with partially overlaid molecular model (V = –0.03 V, I = 2.2 nA). **e**, PTCDA intermediates colligated with gold atoms into linear polymers between PPP polymers at 220 °C (V = –2 V, I = 0.05 nA). **f**, High-resolution STM image with partially overlaid model of the polymer (V = –0.1 V, I = 1.8 nA). **g**, STM image of graphene-like nanoribbons comprising four- and eight-membered rings formed after C-Au bond cleavage and cyclodehydrogenation at 360 °C (V = –1.8 V, I = 0.6 nA). Inset: The ribbon length distribution based on the analysis of a total of 135 ribbons. **h**, High-resolution STM image with partly overlaid molecular model of the graphene-like nanoribbon (V = –1.6 V, I = 0.3 nA).

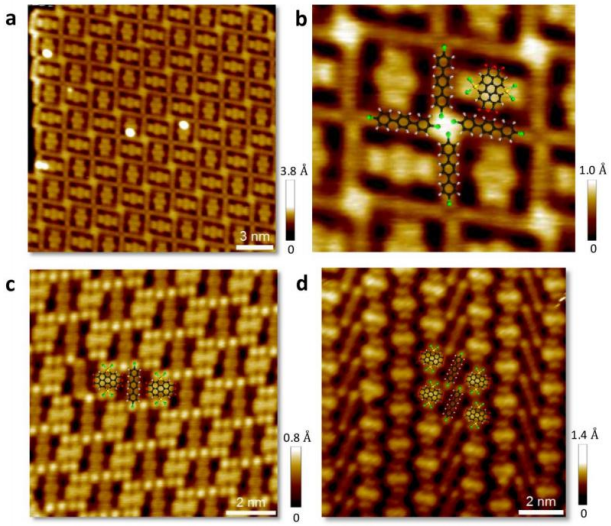

Figure 3 | Different types of self-assembled superstructures at different molecular coverages. a, STM image of a well-ordered network formed by PTCDA-Au_2-Br_4 hybrids and DBTP molecules at about 1:2 ratio (V = –2 V, I = 0.1 nA). **b**, STM image showing a quartet node of windmill shape formed by four DBTP molecules. **c**, STM image obtained at about 1:1 growth ratio of Br_4-PTCDA molecules : DBTP molecules (V = –1.6 V, I = 0.3 nA). **d**, STM image of PTCDA-Au_2-Br_4 hybrids and DBTP molecules at about 2:1 ratio (V = –2 V, I = 0.1 nA).