## Unravelling the growth mechanism of (3,1) graphene nanoribbons on a Cu(111) surface

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Over the two past decades, on-surface covalent synthesis of organic nanostructures, has been widely investigated in the aim of fabrication of molecular electronic components and functional nanomaterials, owning to the Scanning Probe Microscopy monitoring which enhanced the synthesis comprehension at the atomic-scale size precision. Graphene nanoribbons (GNRs) are 1D graphene stripes that are widely investigated due to their remarkable electronic properties compared to 2D graphene. Thermally-induced reaction using nonhalogenated 9,9'-bianthryl precursor lead to chiral (3,1)-GNRs, but only on a copper surface. After few controversies, the currently accepted reactional mechanism for the growth of chiral (3,1)-GNRs on a Cu(111) surface suggests first thermal annealing for the generation 2,2'-diradical species through surface-assisted dehydrogenation. Then, the formed radicals stabilize into organo-metallic 1D protopolymer on the surface. [1] Further heating gives the targeted chiral (3,1)-GNR as result of ring-closure driven by a cyclodehydrogenation. Most of the reaction intermediates involved in this mechanism have been observed. Here, we investigate the growth of laterally functionalized (3,1) chiral GNRs by thermal-induced reaction of 10,10' di(aryl)-9,9'-bianthryl on a Cu(111) surface under UHV by scanning tunneling microscopy (STM). We find that the growth of GNRs is not possible when the 10,10' positions of the starting building blocks are substituted by aryl groups. Therefore, we revisit the commonly accepted reaction mechanism accounting for the growth of (3,1) GNR on a Cu(111) surface to explain this phenomenon.[2]



Figure: a) NRG-cyanophenyl precursor, b) the STM image of supramolecular network on Cu(111) (V=-2.2 V, I=10 pA, 30x30nm<sup>2</sup>) and c) interface after thermal annealing of 1h at 673 K (V=1.8 V, I=10 pA, 40x40nm<sup>2</sup>).d) Completed reaction mechanism for the growth of (3,1) GNR induced by a two-step annealing of BA molecules on a Cu(111) surface. The formation of 10,10'-biradical (in red), followed by radical transposition, is added as initial step.

## References

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