On-Surface Synthesis of 2D Porous Organic Covalent-Nanoarchitectures

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Abstract (Century Gothic 11)

Engineering two-dimensional (2D) covalent carbon-based nanoarchitectures has received tremendous attention during the resent years. We investigate on-surface bottom-up synthesis to create patterned graphene nanoarchitectures via Ullmann coupling. Star-shaped 1,3,5-Tris(4-iodophenyl)benzene molecules self-assemble into halogen-bonded structures on graphite [1]. In contrast, our STM measurements reveal that on-surface synthesis of covalent nanoarchitectures is competing with the growth of self-assembled halogen-bonded structures when this molecule is deposited on Au(111) in vacuum [2]. We show that the molecules form covalent polygonal nanoachitectures at the gold surface step edges at low coverage. With coverage increasing two-dimensional halogen-bonded structures appear and grow on the surface terraces. At high coverage the competitive growth between the covalent and halogen-bonded nanoarchitectures leads to formation of a two-layer film above one monolayer deposition. For this coverage, the covalent nanoarchitectures are propelled on top of the halogen-bonded first layer.
We then investigated the on-surface synthesis of covalent nanoarchitectures of star-shaped 1,3,5-tris(3,5-dibromophenyl)-benzene molecules on Au(111). This molecule has two bromine atoms at the extremity of each arm. At room temperature, the molecules self-assemble into a porous halogen-bonded network [3]. One-covalent-bond dimers appear on the surface after annealing at 145 °C. One-covalent-bond chains are created after annealing at 170 °C. One-covalent-bond hexagons as well as two-covalent-bond dimers are appearing on the surface after annealing at 175 °C. Annealing at 275 °C leads to the formation of a porous 2D hexagonal two-covalent-bond nanoarchitecture. STM images show that the number of intermolecular covalent bonds increases as the temperature rises, Fig.1.

References

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[2] D. Peyrot, F. Silly, ACS Nano 10, 5490-5498 (2016)
[3] D. Peyrot, M. G. Silly, F. Silly, Phys. Chem. Chem. Phys. 20, 3918-3924 (2018)
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Figures

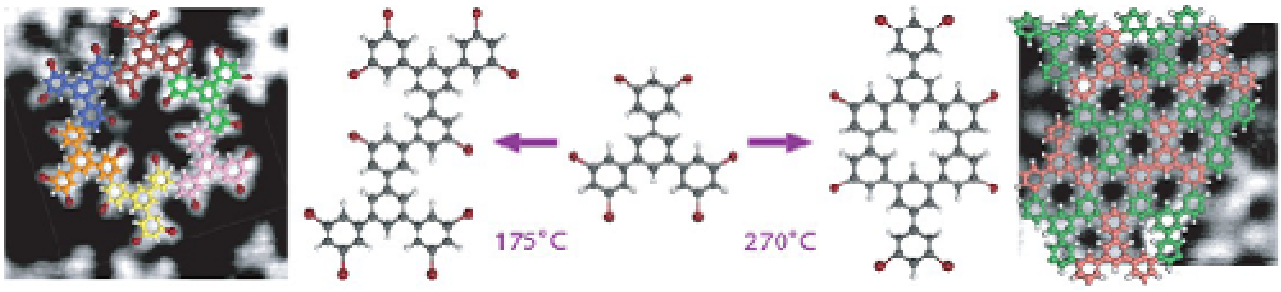

Figure 1: Hierarchical formation of porous structure using bromine-compounds on Au(111). [4]