Factors Hindering Nanoporous Graphene Formation in Favor of Metal-Organic Networks

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The on-surface bottom-up synthesis of nanostructured graphene, such as graphene nanoribbons (GNRs) and nanoporous graphenes (NPGs), enables precise control of electronic properties, from semimetals to semiconductors, making these materials promising for flexible nanoelectronics and quantum computing. This synthesis typically follows a two-step reaction route driven by annealing and the catalytic action of the metallic substrate, with the final architecture determined primarily by the design of molecular precursor (1).

We first combined experiments and DFT to examine how the shape and halogen-substitution pattern of a triphenylene-based molecule influence its vibrational and electronic properties (2-4). The molecule was then deposited under UHV on (111)-coinage substrates and imaged by room-temperature STM, as a potential precursor for NPG growth via a two-step on-surface reaction. However, geometric confinement and steric hindrance between neighboring molecules prevent the dehalogenated precursors from approaching closely enough to form C–C bonds, suppressing the initial Ullmann coupling and favoring metal–organic networks instead (see Figure 1).

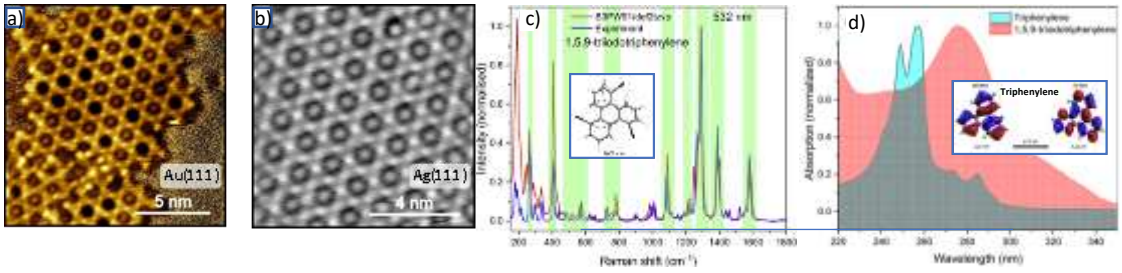

Figure 1: *RT-STM images of metal-organic network formed by triphenylene derivative on Au(111) and Ag(111) surfaces held at 100 °C and 150 °C, respectively. Scanning parameters: (a) 15x15 nm², V_b = 1.7 V, I_t = 7 pA; (b) 10x10 nm², V_b = -2.0 V, I_t = 10 pA. Raman (c) and absorption spectra (d) of triphenylene and triiodotriphenylene.*

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