On-Surface Synthesis of Two-Dimensional Coordinated Nanoporous Networks

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On-surface synthesis has been widely explored to prepare low-dimensional materials and control their functionality at the atomic and molecular levels [1]. A plethora of on-surface reactions can be employed to build such nanostructures, e.g., the C-H activation, Ullmann, and Sonogashira reactions, among others [2]. One of the main challenges is synthesizing a low-dimensional material with long-range and defect-free domains. Therefore, within the bottom-up methods, coordination chemistry has a noteworthy efficiency to build well-ordered metal-organic frameworks (MOFs) with such properties [3]. Herein, we investigate the adsorption of organic molecules with pyridyl end groups on Cu(111) using scanning tunneling microscopy (STM) and density functional theory (DFT). The honeycomb nanostructure formed during room temperature deposition of 1,3,5-tris[4-(pyridin-4-yl)phenyl]benzene) (TPyPB) is stabilized by the presence of Cu adatoms. The growth dynamics change upon adsorption on the surface at 400 K, trapping the molecules on the organic adlayer. The deposition of (1,3,5-tris[4-(pyridin-4-yl)-[1,1'-biphenyl])benzene) (TPyPPB) at room temperature leads to vitreous structures, which rearrange upon annealing at 400 K. After annealing at 420 K a complex arrangement in a flower-like appearance comprising a mix of two- and three-fold coordinated Cu centers emerges. In addition, a honeycomb nanostructure is composed of low-defect and long-range domains. As observed in the smaller precursor, the hexagonal networks are stabilized only in the presence of Cu adatoms. Upon annealing, at temperatures above 420 K, a new phase emerges composed of high molecular density motifs, so-called diamonds.

Acknowledgments: This work was financially supported by FAPESP (2021/04411-1), CNPq, and CAPES (627946/2021-00).

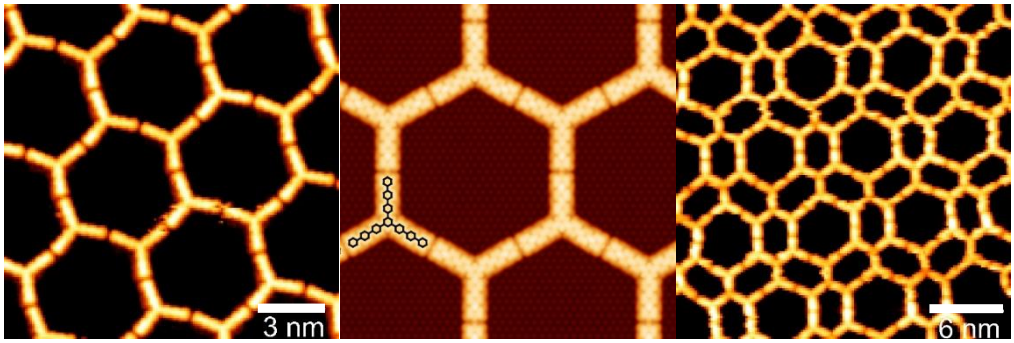

Figure – a) STM image of TPyPPB MOF on Cu(111). b) Corresponding DFT simulation. c) STM image for the Flower-like MOF.

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