

THERMALLY INDUCED SURFACE POLYMERIZATION OF A PERYLENE DERIVATIVE ON Cu(111)

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The fundamental size limits for the fabrication methods of the microelectronic industry will soon be reached. Molecular and atomic self-assembly is a promising alternative route to overcome these mid-term problems with the aim to produce even smaller functional systems with nanometer dimensions on atomically well-defined surfaces. The concepts of supramolecular chemistry have been successfully applied to obtain impressive results for molecular self-assembly on surfaces. Mostly, non-covalent interactions like metal coordination, hydrogen bonding or dipolar coupling have been exploited to create extended supramolecular patterns in variable dimensions. The most common approach to “control” these structures relies mainly on the sophisticated design of the molecular functional groups, which make use of the properties inherent to the molecules.

In this work we present a different approach. A thermally-induced surface-assisted reaction is reported which modifies the endgroups of a perylene derivative (TAPP) [1] (*Figure 1a*). These changes result in different surface assemblies where the following molecular interactions are observed [2]:

- i) At room temperature, TAPP forms a closed-packed assembly on Cu(111), where the intermolecular interactions are based upon van-der-Waals forces (*Figure 1b*).
- ii) After annealing to 150°C, the molecular interactions are changed into a metal coordinated rectangular network. The obtained porous network is commensurate to the underlying Cu surface, where the organic molecules coordinate to Cu atoms through the lone pairs of their nitrogen atoms (*Figure 1c*).
- iii) Higher annealing temperatures (above 240°C) conspicuously modifies the molecules on the surface and a surface induced tautomerization process leads to covalently linked polyaromatic chains (*Figure 1d*). It will be shown that these chains are extremely stable and can be laterally manipulated by the STM tip.

References:

- [1] T. Riehm, G. DePaoli, A. Konradsson, L. de Cola, H. Wadepohl, and L.H. Gade. *Chem. Eur. J.* **2007**, 13, (2007) 7317.
- [2] M. Matena, T. Riehm, M. Stöhr, T.A. Jung, and L.H. Gade. *Angew. Chem. Int. Ed.* **2008**, 47, (2008) 2414.

Figures:

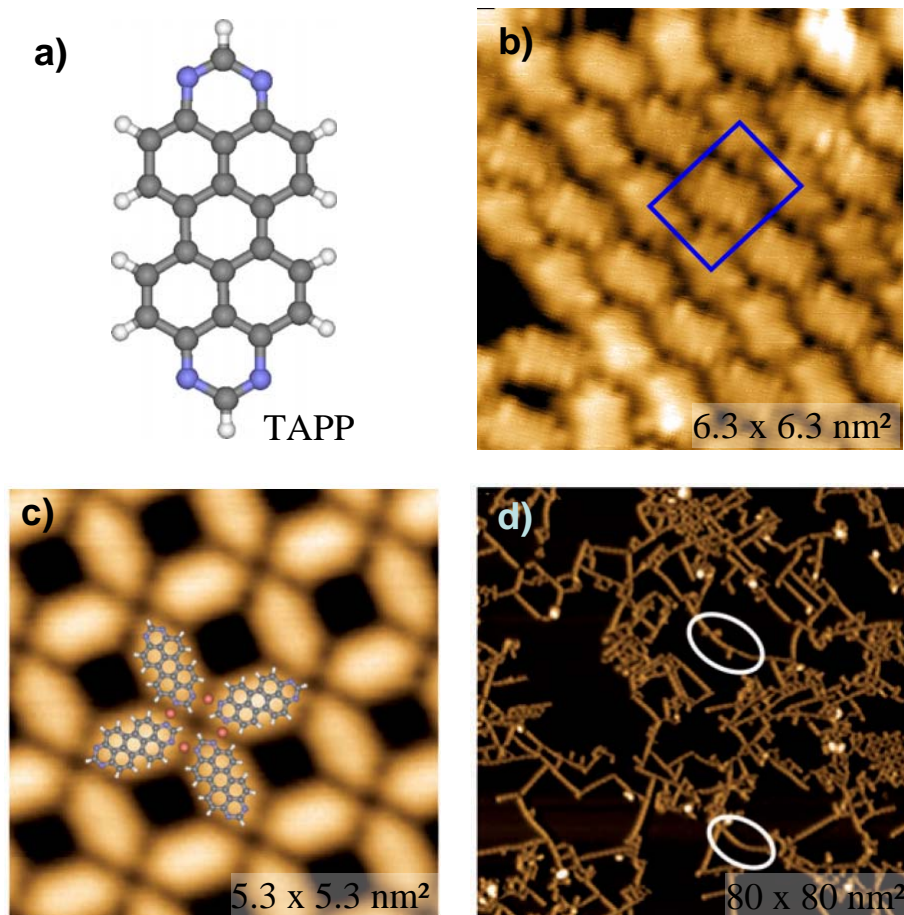


Figure 1: Different molecular assemblies of TAPP deposited on Cu(111) obtained by annealing to different substrate temperatures. **a)** Scheme of the TAPP molecule. **b)** Closed packed assembly formed at RT assembly. **c)** Porous network after annealing to 150°C. **d)** Covalent chains formed after annealing to 240°C. All STM images have been acquired at 77 K. The image size is indicated in each picture.