

**2D POLYMERIZATION OF PLANAR MOLECULAR NETWORKS.**

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Self-assembly of molecules on surfaces directed by different supramolecular interactions has been widely explored. There are striking examples of molecular surface structures, whose formation is driven by metal co-ordination[1], dipolar coupling[2] or hydrogen bonding[3] interactions. In contrast to these examples, our aim is the formation of covalently linked planar structures by means of polymerization confined in one or two dimensions.

The compound 4,9-diaminoperylene-quinone-3,10-diimine (DPDI) we investigated belongs to a class of compounds which serve as precursors for the production of photovoltaic devices. Recent investigations using differential thermoanalysis and gravimetry demonstrated that bulk DPDI can polymerize releasing ammonia. Inspired by this observation, we tried to exploit the formation of covalent networks on metallic surfaces and to check the feasibility of such an approach for the formation of stable polymer-nanostructures.

For this purpose, thin films ( $\leq 1$  ML) of DPDI were prepared on Ag(111) and Cu(111) by evaporation in a UHV setup. In a first step, the supramolecular arrangements were analyzed with our home-built STM. We found a condensed phase with a rectangular unit cell on both substrates if the coverage was in the range of 1 ML. After annealing to 300°C, a rearrangement of the DPDI molecules into a rhombic unit cell structure was observed. This symmetry change was accompanied by the appearance of a new structure linking the individual perylene groups which we identify as covalent bonds in our detailed study. Further evidence, in favour of a covalent bond formation is provided by the shortening of the intermolecular distance of the ad-molecular patterns after the thermal activation. We identify these structures as arrays of 1D polymer rows covering extended areas of the substrate.

For lower coverage in the range of 0.3 ML, only a mobile phase was detected before annealing. However, upon annealing to 300°C a stable 2D network with a honeycomb-like structure was observed (Fig. 1). This structure conveniently matches the angles and distances expected for the chemically feasible polymer structure shown in the inset of the figure.

Our work shows that the polymerization of DPDI on metallic surfaces is well suited for building stable polymer structures in a bottom-up process. These 2D networks shall be used as template structures for second stage molecular adsorption by C60. In our case, amines and perylenes have been used as chemical 'building blocks' for 2D polymers. But similar systems e.g. using different pi electronic systems can be easily imagined on the basis of other chemically well established polymerization reactions.

**References:**

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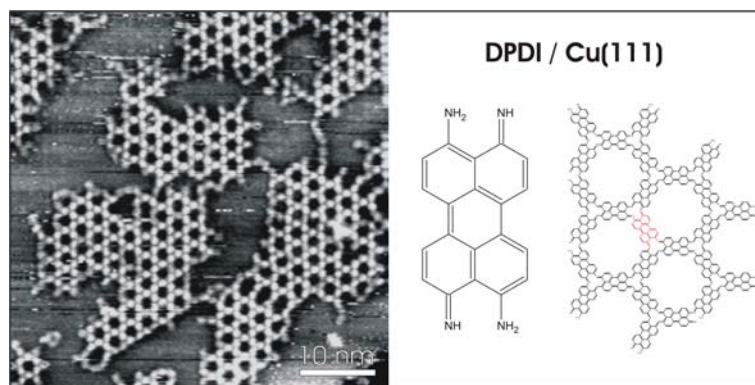
**Figures:**

Fig. 1 Covalent network of DPDI/Cu(111) after 2D polymerization.