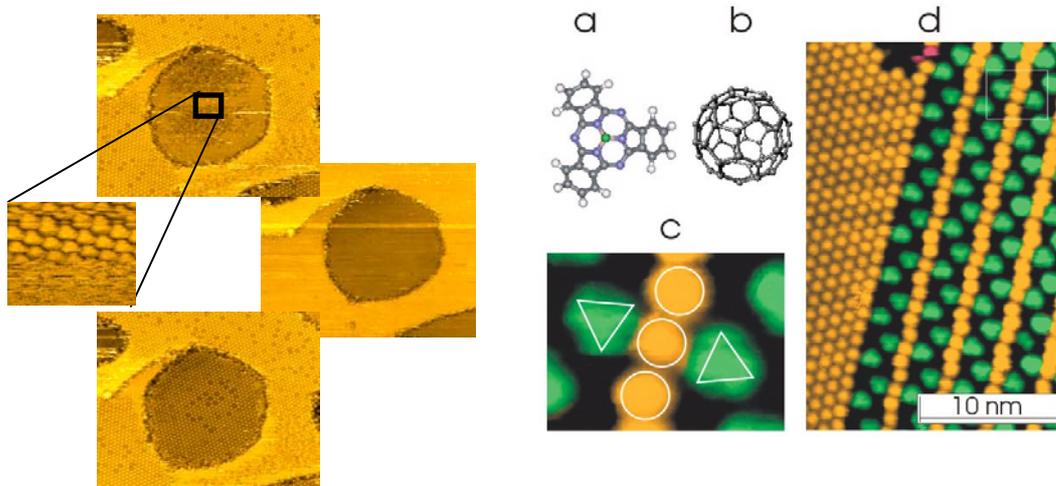


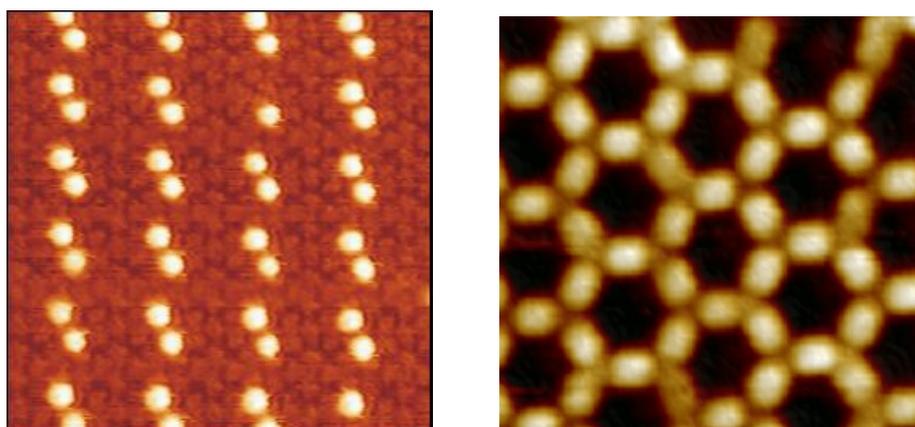
## Molecular and Supra-Molecular Self Assembly: All the Phenomena of Condensed Matter Physics projected into 2 Dimensions.

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One of the key challenges in molecular machines and devices is the reproducible assembly of functional units in an addressable way e.g. in 2D arrays at surfaces. Using a variety of different molecules with specifically designed structure, increasingly complex functional layers have been manufactured and explored. Selective molecular interaction is the generic origin of molecular self assembly [1] and a variety of different mechanisms have been identified: Selective chemical bonding [2], conformational bi-stability [3], and 2D phase behaviour [4] produce distinctly different functional layers. Binary molecular systems which involve longer range dipole forces and entropic mobility provide the basis for an increased periodicity [5]. In conjunction with a conformational mechanism the spacing between individual supramolecular units has very recently been increased to 7.2 nm [6]. Going beyond supra-molecular assembly extended networks have been created by a thermally activated chemical reaction [7] and have been used as a template for supra-molecular organisation of ad-C60 molecules. Most recently the first successful assembly of extended molecular layers on insulator thin films has been demonstrated [8]. All these examples have in common that the supra-molecular structures are extremely well defined and identical on a level which is impossible to reach by conventional top-down assembly techniques. Following the discussion of the physics and chemistry involved in the formation of these versatile structures I shall review and update the concept of mechanic and electronic 'function' on a single molecular scale.





**Fig. 1a)** : Phase transition reversibly triggered by the tip of an STM: STM images of SubPc/Ag(111) in a vacancy island of monatomic height. *a*) overview of liquid phase (no order). During scan in a small subregion (*b*), the molecules order in an hcp pattern (*c*), while scanning at negative bias (*d*) erases the structure resulting again in the fluid phase (as *a*). Tunnel parameters: *a*), *c*) 90 nm x 90 nm,  $I=10$  pA,  $U=1,2$  V, *b*) 11 nm x 11 nm,  $I=10$  pA,  $U=1,2$  V, *d*) 90 nm x 90 nm,  $I=10$  pA,  $U= -1,2$ V. All images were acquired by scanning from bottom to top. **Fig. 1b)**: Self-intermixed phases *a*: Structure of SubPc. *b*. Structure of C<sub>60</sub>. *c*: Artificially coloured STM image of the basic unit of the molecular chain pattern with superimposed schematic shapes (SubPc green, C<sub>60</sub> yellow). *d*: Artificially coloured STM image of a monolayer of intermixed molecules on Ag(111). On the left hand side, close packed C60 overlays are recognised [4] (imaged area, 17 x 25 nm). The bare substrate areas appear dark. *e*: Coexistence of two different intermixed patterns, labelled I and II (image area, 34 x 34 nm). On the right hand side, the chain phase (I) and on the left hand side, the hexagonal phase (II) is observed. Random tip excursions of single molecular height (III) are visible between the two ordered regions and are identified as mobile molecules in a 2D gas phase [3]. **Fig. 1c)** Supramolecular patterned surface by cooperative self assembly of C60 and a Porphyrin. Individual C60 are visible in the second molecular ad-layer. The affinity of the C60 to the underlying porphyrin layer is governed by a cooperative mechanism which involves conformational flexure. **Fig. 1d)** Oligo-perylene Network which is formed by a dedicated covalent reaction activated at elevated Temperatures after molecular adsorption. Hexagonal pockets allow for novel functional properties.

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