Exploiting template surface and end-group functionalities to guide the self-assembly of specific supramolecular architectures

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The future fabrication of nanoscale devices will critically depend on the controlled selfassembly of surface-supported functional supramolecular structures. A well-established procedure is the tailoring of intermolecular interactions by an appropriate choice of molecular building blocks with suitable and complementary end-group functionalities [1]. Another approach is the use of nanostructured template surfaces exhibiting preferential adsorption sites [2-4]. A promising strategy is to use a combination of these approaches to guide the selfassembly. The challenge, however, is to modify and apply the recipe depending on the targeted specific structure.



Figure 1 a), b) and c): Chemical of PTCDI, BDATB and structures DATB. respectively. d) Low temperature (50 K) STM image of the resulting bi-component structures after codeposition of the 3 molecular species on the Au(111) surface (-2.0 V, 0.10 nm^2). nA, 50x50 Upper inset: Supramolecular structure within a BDATB + PTCDI domain. (-2.5 V, 0.11 nA, 10x10 nm²). Lower inset: Supramolecular structure within а DATB + PTCDI domain (-2.0 V, 0.13 nA, 13x13 nm²). Suggested structural models are superimposed.

We recently reported on the successful fabrication of surface-supported bimolecular wires and ribbons by complementary hydrogen-bonding of the two-fold symmetric 1,4-bis-(4,6-diamino-1,3,5-triazine)-benzene (BDATB) (Fig.1a) and perylene tetra-carboxylic di-imide (PTCDI) (Fig.1b) moieties on a vicinal gold template surface [5]. Here we discuss how the co-deposition on a Au(111) surface of a similar, but non-symmetric species; (4,6-diamino-1,3,5-triazine)-benzene (DATB) (Fig.1c) affects the self-assembly and leads to significantly different supramolecular structures. By means of scanning tunneling microscopy (STM) we have investigated the superlattice structures of bi-component domains containing either BDATB and PTCDI, or DATB and PTCDI (Fig.1d). The structures of these domains present distinct properties. We find that co-deposition of the two closely related DATB and BDATB species leads to phase separation (Fig. 2a). Each of the two species self-assembles into different, rather complex, temperature-dependent, single-component supramolecular

structures (Fig. 2). The electronic properties of the diverse entities will be discussed based on data derived from scanning tunneling spectroscopy experiments.



Figure 2 STM images of the supramolecular structures formed by BDATB and DATB on Au(111). a) Zoom into a region with a boundary between a pure DATB domain and a pure BDATB domain (-2.0 V, 0.13 nA, 13x13 nm²). Suggested models are superimposed. b) to g): STM images illustrating the various supramolecular structures formed by DATB on Au(111). (all STM images: $10 \times 10 \text{ nm}^2$).

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