

Supramolecular Self-Assembly Of Linear Polyarene Molecules With Complementary Imide And Amine End Groups

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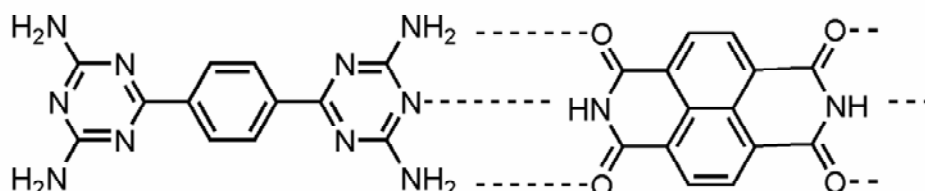
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The process of self-assembly of large functional molecules on surfaces is the single most important step in creating thin films of complex organic molecules for a number of applications in molecular sensing, enantioselective catalysis and recognition structures, and in the rapidly developing fields of molecular devices, such as optoelectronic and logic circuits [1]. In order to use molecular layers in laterally structured arrangements, i.e. in device applications, the control of supramolecular self-organisation on surfaces is of central importance. In supramolecular chemistry, molecules are designed and synthesized to interact specifically with other molecules or to aggregate forming particular structures. Our approach uses vicinal surfaces and one-dimensional templates with the aim of introducing additional one-dimensional anisotropies in two-dimensional supramolecular structures in a controlled way. Using powerful surface sensitive techniques, such as STM, photoemission and NEXAFS, as well as theoretical calculations, we aim to understanding the driving forces (energy) and the parameters (kinetics) that define the supramolecular self-assembly process.

Within this particular collaboration we have synthesized a pair of molecules with linear symmetry and two-different end groups, namely pyromellitic dimide (NTCDI) and benzodiguanamine (BDG), a new molecule of the diaminotriazine family close to the melamine (see the figure). Our final purpose is tuning one-dimensional supramolecular assemblies via homogeneous hydrogen bonding between di-imide (NTCDI) and di-amine (BDG) groups. We are currently carrying out a combined experimental and theoretical investigation in a variety of homodimer and heterodimer structures, which are observed to form on a Au(111) surface at different molecule coverage. These are BDG chains pinned by the elbows of the herringbone reconstruction, two-dimensional supramolecular homodimeric structures, as well as heterodimeric chains that pack forming an orthorhombic crystal. Experiments include STM, NEXAFS and valence-band as well as core-level photoemission. In parallel, we calculate the geometry of isolated molecules, dimers and tetramers using the GAUSSIAN code, while periodic supercell DFT calculations using the VASP code are done to include the effect of the Au substrate.



Hydrogen bonding between benzodiguanamine (BDG, left) and pyromellitic dimide (NTCDI, right). Heterodimeric chains are observed to self-assemble on Au(111) for a 50% mixture of both molecules.

[1] "Molecular Electronics: Science and Technology", eds. A. Aviram and M. Ratner, Annals of the New York Academy of Sci. vol. **852**, New York 1998; Heath et al., Science **280**, 1716 (1998); Chen et al., Science **286**, 1550 (1999); Collier et al., Science **289**, 1172 (2000); Science **295**, 2395-2421 (2002).