Self-Assembled Monolayers of Non-Planar Aromatic Carboxylic Acids on Ag

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Aromatic carboxylic acids (ArCAs) have been demonstrated to form highly organised monolayers of upright standing molecules on metal surfaces such as copper and silver by adsorption from solution [1-6]. Silver, in particular, promises a flexible design of layers as intermolecular interactions can dominate over substrate-molecule interactions, thus, overcoming the issue of lattice mismatch between the molecular layer and the underlying substrate. An illustrative example is the assembly of benzenetribenzoic acid where intermolecular interactions involving both π-systems and carboxylic acid moieties yield layers which exhibit a pronounced row structure and feature nanotunnels [5].

Since, so far, only rod-like or planar molecules have been investigated, the question arises of how a non-planar geometry affects the ability of molecules to establish π-interactions and hydrogen bonding and, thus, their propensity to form highly organised layers. The two molecules (H2MDB, H4MTB see Fig. 1a) presented here are homologous derivatives of tetraphenyl methane. Prepared on a bilayer of Ag on Au(111)/mica the monolayers were characterised by ambient scanning tunnelling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy.

Both compounds form highly crystalline SAMs with analogous structures where two carboxylic acids groups bind to the Ag surface in a bidentate fashion. This bipodal adsorption is notably different from the other ArCAs on Ag studied so far as they all favour a monopodal adsorption geometry. An unexpected behaviour is observed when the non-planar molecule H2MDB (Fig. 1b) is coadsorbed with the linear molecule biphenylcarboxylic acid (BPCA, Fig.1a). Contrasting the typical behaviour of binary SAMs to either form a random mixture or separate phases of molecules, a highly regular pattern emerges (Fig. 1c) which consists of one molecule wide rows of BPCA alternating with rows of H2MDB. The results presented here are a further manifestation that ArCAs on Ag represent a promising platform for the design of SAMs.

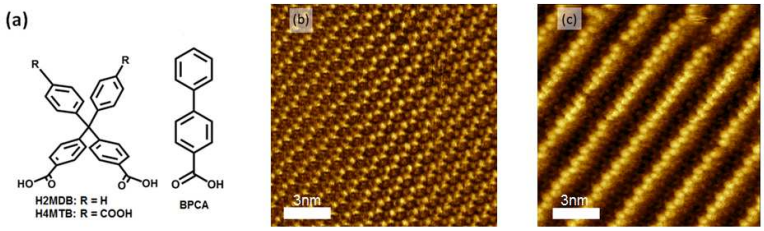

Fig. 1: Structures of molecules investigated (a) and STM images of a pure layer of H2MDB (b) and coadsorbed with BPCA (c).

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