STM manipulation of molecular moulds on metal surfaces

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Molecular Landers are a class of compounds in which an aromatic board is decoupled from the underlying substrate via bulky spacer groups. They have attracted considerable attentions as molecular wires, light-driven nanocars, in particular due to the special capability by trapping metal atoms beneath into nanostructures[1,2]. However, except those pure-ordered short Lander chains, the attempt on 1D assembly of the Lander moulds has been only succeeded when applying special templates which unfortunately limits the future application.

By means of scanning tunneling microscopy (STM) imaging and manipulation, the morphology and anchoring of a specially designed Lander-type molecule, bis(diaminotriazine) (DAT, $C_{64}H_{68}N_{10}$) (Fig. 1(a)) is studied on Cu(110) and Au(111) surfaces under ultrahigh vacuum (UHV) conditions. Different electronic contact configurations of individual DAT molecules at step edges of Cu(110) substrate can be achieved and modified in a controlled manner by STM manipulation, including lateral translation, rotation, and pushing the molecule to an upper terrace. Through the comparison of manipulation of individual DAT on Cu(110) and Au(111) surfaces, we probe the qualitative molecule-substrate interaction directly, indicating that the diffusion barrier of single DAT molecules on Au(111) is smaller than that on Cu(110) and providing relevant information to the substrate selection for the self-assembly of DAT.

Fig. 1(b) presents a high-resolution STM image of a DAT molecule on Cu(110), showing four bright lobes in a rectangular shape (11.0 Å × 6.5 Å), and some sub-protrusions in the centre. The same morphology of the DAT molecule is depicted on the Au(111) surface (Fig. 2(b)). We tentatively interpret that each bright lobe corresponds to tunneling through one of the four *tert*-butyl groups, while the sub-protrusions may be attributed to the hexa-phenyl rings, which are connected with the central benzene by σ bonds. There is, however no obvious feature in the recorded STM images that can be attributed to the diamino-pyridine group. Theoretical simulations have been performed using elastic-scattering quantum chemistry (ESQC) [3] after having relaxed the molecule on the surface with molecular mechanics MM4(2003) code [4]. The STM images are compared with theoretically calculated STM images using the ESQC approach. From Figure 1(c) and Figure 2(c), it is seen that the contribution of diamino-pyridine groups to the tunneling current is apparently minor, consistent with the experimental findings, which confirms the interpretation above of the individual DAT molecule. Taking into account the electronic gap of DAT (2.05 eV), a calculation of the different molecular orbital shows that the highest occupied molecular orbital is imaged at the operating energy.

Lander B consists of a central polyaromatic unit, two imide functional groups on opposite sides and four *di-tert-butyl-phenyl* (DTP) spacer leges (Figure 3(c)). Figure 3(a) and 3(c) present the experimental and simulated STM images of a single Lander B molecule respectively, which are nicely consistent with each other. The dimension of the four bright

protrusions is approximately 14.5 Å long and 9.5 Å wide, attributed to tunneling through the DTP groups. Since the molecular core is lifted away the substrate (Figure 3(d)), its contribution to the tunneling current is rather minor. Similar to Lander A, the imide groups of Lander B also allow the HB between neighboring molecules, where the neighboring Lander B adopts a head-to-tail arrangement. The double N-H···O HB between imide functional groups.

References:

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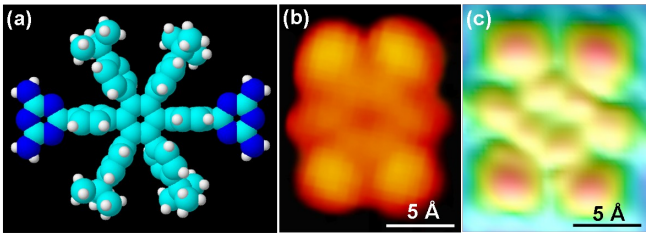

Figure 1: (a) Space-filled model of bis(diaminotriazine) (DAT) molecule ($C_{64}H_{68}N_{10}$). It consists of a benzene ring connected with four *tert*-butyl groups and two diamino-pyridine groups by σbonds, where the carbon, hydrogen and nitrogen atoms are represented in pale blue, white and blue, respectively. (b) A typical high-resolution STM image of a DAT molecule on Cu(110). (sample voltage, -1.73V; tunneling current, -0.66 nA) (c) ESQC-simulated STM image of the DAT on Cu(110) as the same tunneling conditions as the experimental result in (b).

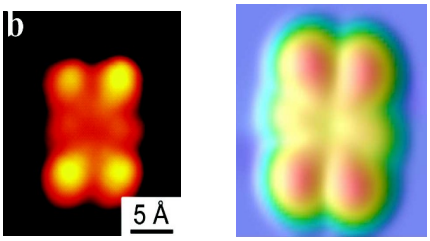

Figure 2: (b) A high-resolution STM image of a single Lander A (DAT) on Au(111). (I_t=0.32 nA, V_t=1487 mV). (c) EHMO-ESQC simulated image of Lander A on Au(111) at the same tunneling conditions as in panel (b).

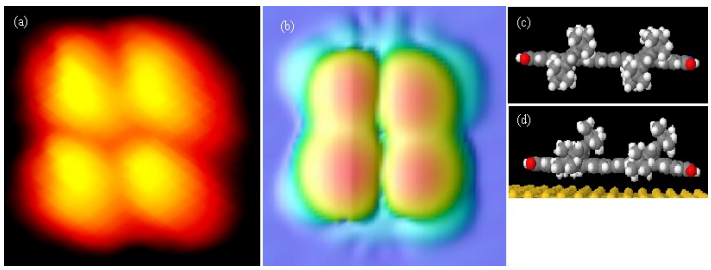

Figure 3 :. (a) A high-resolution STM image of a single Lander B on Au(111). (I_t=0.26 nA, V_t=1239 mV). (b) ESQC-MM4 simulated image at the same tunneling conditions as in panel (a). (c) The anticipated model of space-filling Lander B. Carbon, hydrogen, oxygen and nitrogen atoms are represented in grey, white, red and blue, respectively.