

"Snake-Like" motion of of a single poly-pyrene chain sliding on gold.

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Understanding the motion/dynamics of a single molecule over a surface is a problem of a paramount importance in the design of advanced molecular nanostructures/assemblies capable of meeting specific needs[1]. The interest is better realized by the broad spectrum of promising applications including molecular electronic devices, tribology/corrosion inhibition, and 3D nanopatterning[2]. One possible route to achieve a higher control on molecular diffusion along predetermined pathways would be to access the single-molecule mechanics during their on-surface displacements[3]. This in turn would provide a mean to rationally design molecules with improved assembly/difusion properties. Nevertheless, to date, understanding the interplay between molecule mechanics, surface displacements and dynamics at a atomic level is a highly challenging task since it requires the knowledge of not only the forces needed to manipulate them but also to relate them with particular molecular/atomic motion.

Here we bridge this gap by combining all-atom molecular dynamics simulations with scanning probe microscopy, force spectroscopy in ultra-high-vacuum conditions at 5K to investigate the mechanical response of a single poly-pyrene chain sliding over a gold surface. Pulling and sliding simulations/experiments shows in quantitative agreement show periodic patterns on the force related to the successive detachment of the chain units (~ 0.8 nm) as well as stick-slip modulations over the surface (~ 0.28 nm). Additionally the simulations reveal a surprising complex on-surface dynamics of the molecule where a dynamic balancing between the intra-molecular mechanics and surface comensurability result in a snake like motion of the molecule over the surface. This counter-intuitive motion, also evidenced by force spectroscopy data, is a direct consequence of the low stiffness of the C-C bond inter-connecting the pyrene units allowing the chain to adapt during motion its commensurability with the atomic lattice. Additionally, during the lifting process we also observe a achiral \rightarrow chiral transition arising from both the steric repulsion between successive units and surface interaction (which is evidenced by the helical structure adopted by the lifted segment as shown in the image provided).

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[2] Tao , Feng. Pure Appl. Chem. 80, 45 (2008)

[3] Kudernac, T. et al. Nature 479, 208–211 (2011).

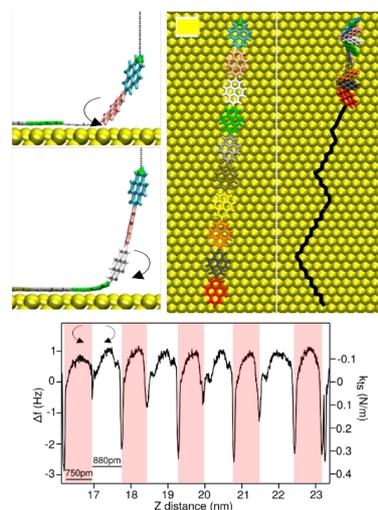


Fig 1: (top) Configuration of a 10-pyrene molecule over Au111, initial and as lifted. Notice the zig-zag pattern followed by the molecule as lifted as well as the helical structure of the lifted segment. (bottom) Force gradient of the normal load obtained as we lift the molecule.