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ARTICLE TYPE

Supporting information

Building layer-by-layer 3D supramolecular nanostructures at the terephthalic acid/stearic acid interface

Experimental techniques

The terephthalic acid and stearic acid molecules were dissolved in 1-phenyloctane (from Sigma Aldrich 99% pure) solvents to produce nearly saturated solutions, respectively. The STM experiments were performed individually under ambient conditions at the liquid/solid interface with a commercial Multimode scanning probe microscope (SPM) system (NanoscopeIIIa,Veeco Instruments, Santa Barbara, CA). For building 3D structures, a droplet of STA wasdeposited on a freshly cleaved HOPG crystal and STM images were recorded at the interface of the 1-phenyloctane solution and HOPG surface. Subsequently, a drop of TPA was deposited on the top of the STA monolayer. The STM tips were mechanically cut from a 0.25 mmPt/Ir wire (80% /20%) and tested on freshly cleaved HOPG surfaces. Several different tips and HOPG samples were used to ensure reproducibility of the results presented below. All STM images were recorded in the constant–current mode under various tunnelling conditions (tunnelling currents: 0.5-1.0 nA, and bias voltages: 0.5-0.8V), and with the sample positively biased. The STM scanner was calibrated from images of clean HOPG using the Scanning Probe Image Processor (SPIP) software (Image Metrology Aps, Lyngby, Denmark).

Figure

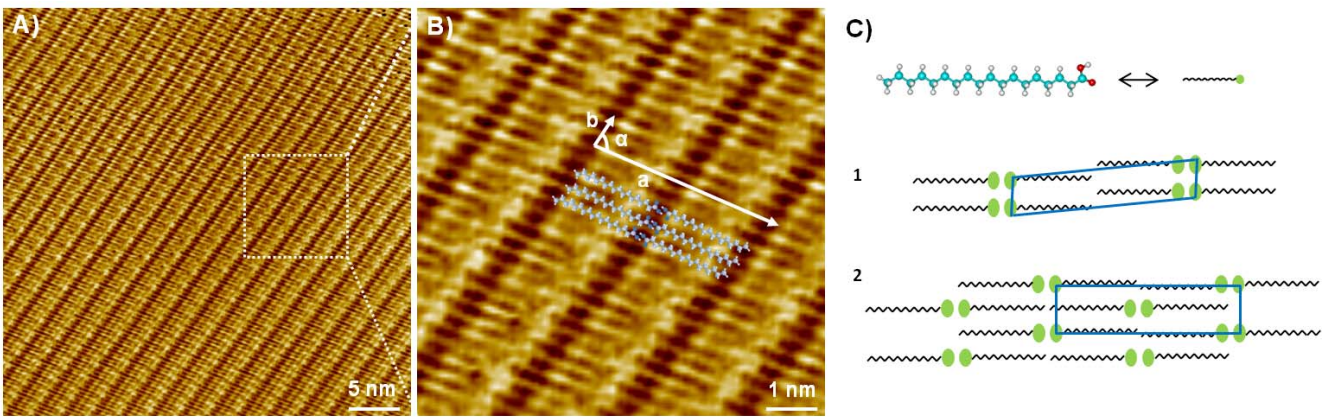

Fig.S1 STM images of STA at liquid/solid interface. (Tunnelling current = 246.3pA and voltages = 991.2 mV) A) A large STM image of STA assemblies on HOPG surface;Inwhite dashed square, the assembling structure with high resolution will be explored.B) The high resolution STM image of STA assemblies and STA model superimposed on the STM image. Unit cell of STA assemblies is a = 5.10 ± 0.3 nm, b = 0.88 ± 0.1 nm, α = 80 ± 5 °.C) Two possible schematic models of STA assemblies.

Stearic acids consist of terminal carboxylic groups and alkane backbones. The terminal carboxylic groups form hydrogen bonds between two neighbouring STA molecules, resulting in the self-assemblies with lamella characteristics. The alkane backbones could provide a hydrophobic venue in these assemblies, which can be used to fabricate the functional interface where the second layer assemblies could adsorb on. A droplet of saturated STA solution wasplaced on the HOPG surface, and then the uniform, large and flat domains were formed with lamella characteristics, as depicted in the STM in Fig. S1A. A high-resolution STM image of thelambella structure is shown in Fig. S1B, which is consistent with the features of STA assemblies reported in theprevious literature[1]. Each bright line corresponds to the single stearic acid molecules on the HOPG surface. The length of the molecules measured in STM images is about 2.27 ± 0.3 nm,

matchingwell with the theoretical values. The unit cell is depicted in Fig. 1B and the lattice parameters determined from the STM images are depicted in Table 1.Long range uniform domains cover most of the HOPG surface and furthermore different domain boundaries were observed with different orientation due to the interaction of the 2D self-assembled STA layer with the underlying graphite substrate. In Fig.S1C, the suggested models were displayed, and model 1 is in agreement with the formation of STA monolayers in STM image we observed, while STA assemblies with model 2 structures were not observed in our STM experiments.

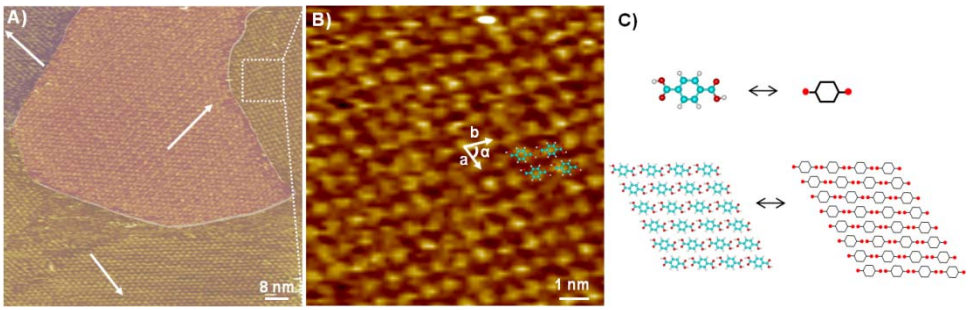

Fig.S2 STM images of TPA at liquid/solid interface (Tunnelling current = 744.7pA and voltages = 865.3mV). A) The STM image of TPA assemblies on HOPG surface in three domains with different orientations;white arrows display the orientations of TPA assemblies on HOPG surface. The high resolution assembling structures of TPA molecules are investigated in white dashed squareB) The high resolution STM image of TPA assemblies and TPA model superimposed on the STM image.Unit cell of TPA assemblies are = 0.85 ± 0.5 nm, b = 0.95± 0.1 nm, α = 70± 5 °.C) The schematic models of TPA assemblies.

Terephthalic acid (TPA) is an aromatic planar molecule with two carboxylic groups which attach to opposite sites of the benzene moiety. TPA is a favourablemolecule to be used in constructinga wide variety of supramolecular architectures on surfaces due to the intermolecular hydrogen bonding between the –COOH groups. In fact, it appears to be facile to obtain a physisorbed monolayer of TPA molecules after depositing one drop of the solution on the HOPG surface. The hydrogen bonds become a dominant driving force to form the well-defined self-assembled monolayer at the liquid/solid interface. Fig. S2A shows a large scale STM image of homogeneous long-range orderedassembly of TPA molecules with three different domains indicated by different colours. These orientations (indicated with three white arrows) of TPA molecular packing reflect the symmetry of the HOPG substrate. To obtain the TPA orientation on HOPG, calibration and drift compensation in the STM images was achieved by acquisition of the atomically resolved HOPG surface at the same spot and with the same scan speed. By varying the bias voltage, STM was operated at manipulation regime where the molecular networks were destroyed/removed by the tip, and the underlying HOPG substrate was revealed. High resolution STM image of TPA assembled structures in one orientation (Fig. S2B) shows that the individual TPA moleculesare closely packedwith each other. Each brightprotrusion in the STM image depicted in Fig. S2B is attributed to one TPA molecule lying flat on the HOPG surface andthelinear arrangement of TPAmolecules areinterconnected *via* hydrogen bonds between the adjacent carboxylic groups.The length of the molecules determined from the high resolution STM images is 0.85 ± 0.5 nm, in very good agreement with the expected length of the TPA molecules. The results of the size of the unit cell of the TPA molecules as measured from the STM images are summarised in Table 1. In Fig. S2C, the proposed molecular model of the assembled TPA molecular structures isdepicted. The assembled structures of TPA molecules in the other two directions are the same as those in Fig. S2B. It is clearly observed that the symmetry of the HOPG substrate enables the TPA molecules to be closely packed in three directions, which is mainly attributed to the interaction between the aromatic planes of TPA molecules and the underlying HOPG surface(π-π interaction).