ChemComm

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ROYAL SOCIETY OF CHEMISTRY

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View Article Online
DOI: 10.1039/C7CC06597C

Journal Name

COMMUNICATION

STM bias voltage-dependent polymorphism of a binary supramolecular network

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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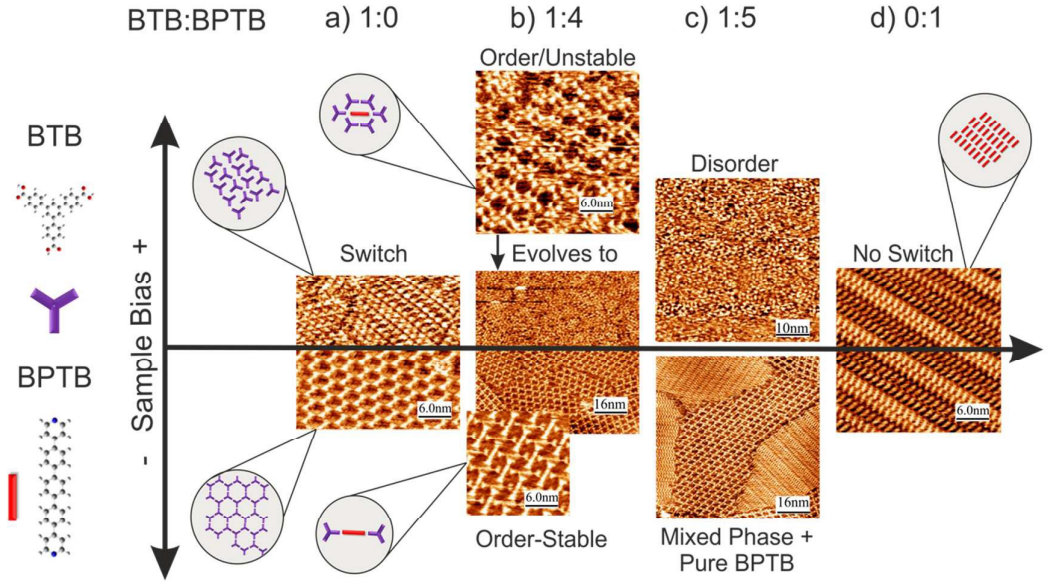
A Scanning Tunneling Microscope (STM) is used to induce a reversible transition between different polymorphs in a binary supramolecular network at the liquid/solid interface. The transition is driven externally by switching the polarity of the sample by positive or negative sample bias potentials. We demonstrate that by mixing bias-sensitive and non-sensitive molecules we gain access to a variety of binary porous structures that can be prepared and reliably actuated for each relative concentration.



Self-assembled 2D supramolecular networks are a promising route towards the precise engineering of nanostructured surfaces.[1,2] Multicomponent,[3,4] chiral[5] as well as peptide-modified surfaces[6,7] are being intensively investigated. Possible applications include capture and release of molecules in host-guest systems,[8,9] surface electronics[10] and catalysis.[11] The ability to tune the size and shape of the supramolecular structure is essential for achieving a desired function and to understand the mechanisms and characteristic energies of the surface interactions at play. Moreover, controlling the po-

Fig. 1: Stick-and-ball model of BTB and BPTB. (a)-(d) STM constant current images in NA on HOPG at different BTB:BPTB ratios and bias sign. (a) Pure BTB, closed (positive bias) and open (negative bias) structure. (b) 1:4 Mixture: Unstable multicomponent polymorph (positive bias) and stable structure (negative bias). (c) 1:5 Mixture: Disordered structure (positive bias) and multicomponent ordered

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DOI: 10.1039/C7CC06597C

structure + pure BPTB islands (negative bias) (d) Pure BPTB, invariant with the bias sign.

lymorphic outcome by an external stimulus such as light[12,13] or temperature[14,15] makes it possible to trigger structural and functional transitions *in situ*. Earlier works, reported on the use of a Scanning Tunneling Microscope (STM) to obtain images of supramolecular networks on appropriate conducting surfaces with sub-molecular resolution and on how to manipulate the surface arrangements of molecules and atoms.[16–19] In a previous work, we used the electric field between the tip of an STM and the sample as an external stimulus to locally manipulate the reversible transition between two different polymorphs of a single-component network at the solid-liquid interface[20]. We have shown that 1,3,5-tris(4-carboxyphenyl)-benzene (BTB) on Highly Oriented Pyrolytic Graphite (HOPG) undergoes an immediate transition from an open porous structure at negative bias to a close-packed polymorph at positive bias and vice-versa (Fig. 1a). In ref [20], we proposed that the conformation of the molecule and therefore the supramolecular outcome was controlled by the orientation of the surface dipole. In particular, the orientation of the surface dipole under positive voltages induce COOH groups to bend toward the surface inducing the molecule into a nonplanar configuration.

In this work, a linear molecule composed of two pyridine groups linked at both ends of a *p*-terphenyl group is studied (4,4'-bis(4-pyridyl)-terphenyl; BPTB) and the possible switching behavior is tested. Pure BPTB molecules in *n*-nonanoic acid (NA) adsorb flat at the liquid-solid interface. They form a supramolecular network by H-bond interactions between N-pyridyl atoms and the H atoms next to the N-pyridyl atoms in the BPTB neighbor molecule (Fig 1d). In contrast to the effect described for the BTB network (Fig 1a), the pure BPTB structure is independent of the sign of the bias voltage (Fig 1d). Unlike BTB, BPTB has no induced dipole moment and is always adsorbed fully parallel to the surface. Moreover, we observe no dependence of the dilution on the polymorphic outcome. Therefore, BPTB is not expected to alter the ordering mechanism acting in the pure BTB system. To investigate this effect, a multicomponent system composed of BTB and BPTB at different mixing ratios (BTB:BPTB) is studied in detail. Different BTB:BPTB solutions were dissolved in NA, deposited on a freshly cleaved HOPG, and measured at the solid-liquid interface using STM at RT. Figures 1 b-c, show the different polymorphs obtained for intermediate BTB:BPTB ratios. When the concentration of BTB is equal or higher than BPTB (5:1, 5:2, 5:3 and 1:1 BTB:BPTB ratios), the typical pure BTB structure is observed: a close-packed structure at positive bias and a porous structure at negative bias. For the BTB:BPTB mixture with an intermediate ratio of 1:4, two bias-dependent polymorphic outcomes were observed. On the one hand, at negative bias, a regular and ordered multicomponent structure is found, as shown in the bottom panel of Fig. 1b. The unit cell contains four BTB and two BPTB molecules as is clearly observed in Figure 2a (network parameters, a = 7.4 ± 0.1 nm, b = 5.7 ± 0.1 nm, a^b = 30±2° (S2)). The structure is independent of the scanning direction. On the other hand, at positive bias, an ordered but metastable structure is observed (Fig. 1b top). The unit cell contains the structural units depicted in Fig. 2b; it includes six BTB molecules and one BPTB (a = 5.9 ± 0.1 nm, b = 5.5 ± 0.1 nm, a^b = 48±1° (S2)). This metastable structure can be observed for up to 15 minutes after sample deposition. The structure then evolves into a disordered phase, exhibiting mostly BTB molecules at the solid-liquid interface (Fig 1.b, time evolution shown in S3). This change over time is attributed to the fact that, at positive bias, this structure is the kinetically favored polymorph and is not thermodynamically stable. Considering the structural change between sequential STM images, the observation of bright moving spots in the image, and the increased noise level during the network evolution, a high diffusive and detaching-reattaching process due to the unstable nature of the network can be assumed.

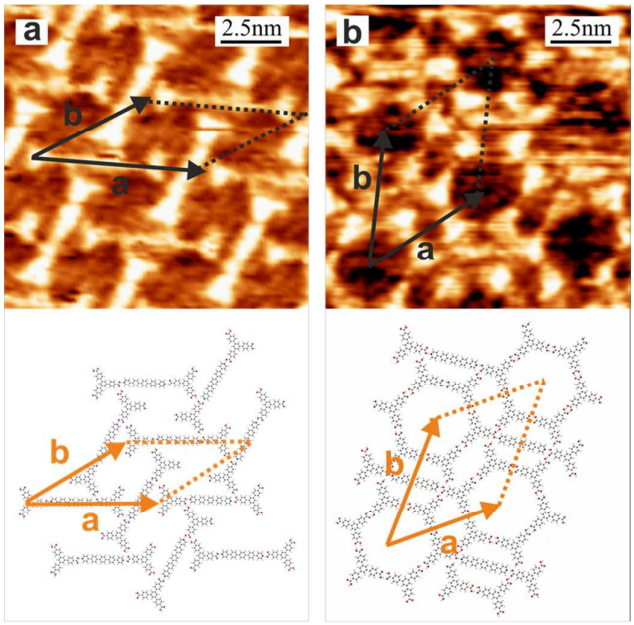

Fig. 2: STM constant current images and the molecular model of (a) multicomponent regular, stable structure at negative bias (-1170 mV, 50 pA) and (b) multicomponent, metastable structure at positive bias (770 mV, 122 pA).

Switching from positive to negative bias immediately and reliably restores the ordered structure within a single scan line (Fig. 3a). The inverse process (Fig. 3b) establishes the disordered structure. In a bias voltage window from about -650 to 400 mV, no molecules can be observed (Fig. 4). Both facts agree with the switching behavior previously found for a pure BTB solution.[20]

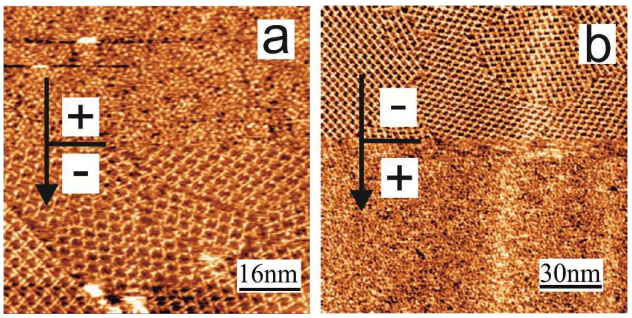

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Fig. 3: Reversible switching behavior of the multicomponent structure. Arrows show the scanning direction. (a) From positive to negative bias, ordered structure appears (850 to -850 mV, 26 pA). (b) From negative to positive bias, the system returns to a disordered state (-830 to 850 mV, 30 pA).

In order to understand the influence of the planar BPTB molecules on the BTB switching processes, several samples with different BTB:BPTB mixing ratios (S4) and dilutions were analyzed (S5). The dilutions investigated span from 5% to 50% (S5). Pure BTB phases, namely closed-packed at positive and open at negative bias, are observed even after minor BPTB addition, albeit with increasing disorder in the positive bias phase. The multicomponent ordered structure at negative bias (Fig. 1.b) appears from a ratio of 1:2. Ratios of 1:4 and 1:5 are found to be the optimal concentrations for the binary supramolecular network, exhibiting the both the positive and negative bias structures, as well as the switching behavior described above. Samples formed with 1:5 ratios exhibit not only the multicomponent structure at negative bias, but also some pure BPTB domains as shown in Figure 1c (S6). As already shown above, a pure BPTB solution (0:1 ratio) exhibits a non-bias-dependent structure. In order to reach a graphical comparison on the structures found according to different variables (such as mixing ratio, dilution, bias and current) we developed a software tool which allows us to tag STM images according to the features they show (Figure 4, S4 and S5). Figure 4 shows the polymorphs (color-coded) and the experimental conditions at which they were observed in a current vs sample bias profile. It also shows that in the bias voltage window from -650 mV to 400 mV, no molecules are clearly observed.

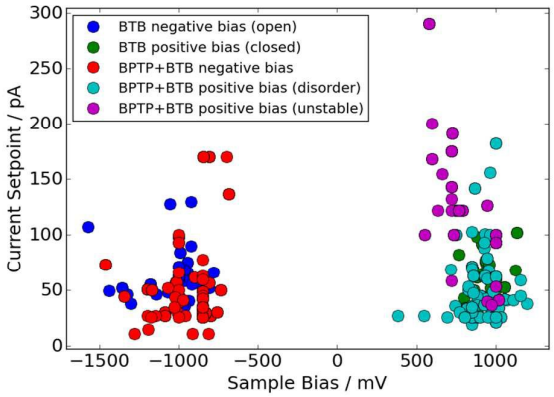

Fig. 4: Parameter ranges in which the respective structures were observed. One point corresponds to one image.

A 2.5-fold BPTB excess is needed to obtain a structure in which only one half of the molecules at the surface are BPTB (Fig. 2a). A fourfold BPTB excess is needed to observe the positive bias structure where only one sixth of the molecules at the surface is BPTB (Fig. 2b). This shows that the surface adhesion of BPTB is much lower than for BTB. However, even though the surface adhesion of BPTB is low, the presence of BPTB in a BTB solution still allows for collective order that can be controlled by the STM bias. At negative bias, the stable structures are the ones diluted in BTB. These observations support our previous claim[20] that the induced local electric field favors different conformation-dependent charge-transfer mechanisms, which lead to different structures, depending on the sign of the bias voltage.

In conclusion, the incorporation of a rigid molecule to a switching supramolecular network allows the creation of binary structures adding complexity and variety to the porous geometries, while keeping a reliable switching behavior. Our work shows the potential for controlling complex multicomponent architectures at interfaces by tuning the local electric field. This design principle will be extended to design pores exposing shapes and functional groups to reversibly catch and release specific guest molecules from solution.

We acknowledge financial support from the project SEED Money Grant "Surface Supported Smart Supramolecular Nanopores" and from the MPI-EPFL Center for Molecular Nanoscience and Technology.

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DOI: 10.1039/C7CC06597C

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