Supporting Information (SI)

STM bias voltage-dependent polymorphism of a binary supramolecular network

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S1: Sample preparation

Method I: Droplets between 20 and 100 µL of a saturated BTB and BPTP solution were diluted with pure *n*-nonanoic acid (NA) in order to obtain the desired concentration. From this diluted stock solution, a 2 µL droplet was pipetted onto a freshly cleaved 1cm x 1cm highly oriented pyrolytic graphite (HOPG) substrate. The HOPG, covered by the liquid, was then placed in a Bruker STM for measurement.

Method II: Desired dilutions of BTB and BPTP were prepared individually as described above. For measuring, a HOPG substrate was cleaved, cleaned and placed in the STM. A 2 µL droplet of pure n-nonanoic acid was placed onto the HOPG substrate and 2 µL of saturated BTB and BPTB solution were added. The 2 µL droplet of NA should balance the loss of solvent due to evaporation and is thus not considered in the calculation of the given dilution values.

No differences in the obtained supramolecular structures between the preparation procedures were observed. For both methods, the STM images were taken at room temperature and immediately after deposition. The STM images that are presented were processed using the WSxM[1] software package. The background was removed by applying a plane fit and flattening filter. Additionally, some images were equalized and cropped.
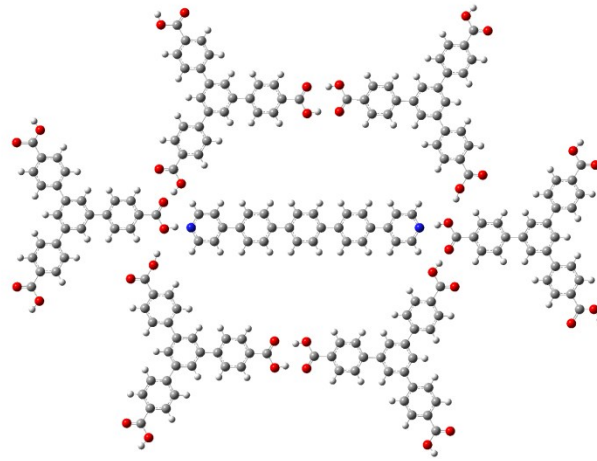
S2: Unit Cells

Unit cell dimensions were measured using the WSxM software. Unit cell models were constructed using optimized models for BTB and BPTB. The desired unit cell was built by maximizing the hydrogen bonds between units.
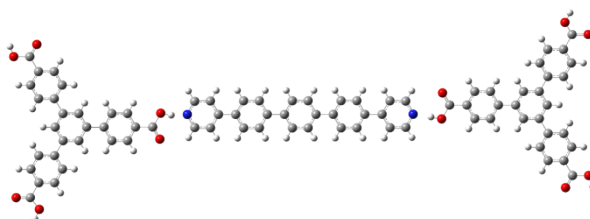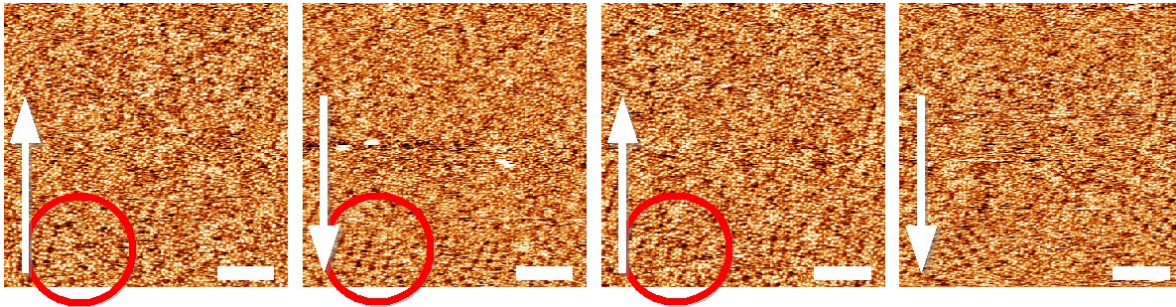

Unit 1: BTB-BPTB-BTB unit cell model that was used to construct the multicomponent structure obtained at negative bias.

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[1] I. Horcas et al., Rev. Sci. Inst., 2007, **78**, 013705.

Unit 2: 6xBTB-BPTB unit cell model that was used to construct the metastable multicomponent structure obtained at positive bias.

**S3: Time evolution of the disordered phase**

S3: STM constant current images of the time evolution of the disordered phase at positive bias. Bias = 1000 mV, I = 93 pA, scan rate 3.00 Hz. Concentration BPTP-BTB 4:1. While continuously scanning the same area, 9 minutes passed. Scale bars are 20 nm. In areas outside the red circles the unstable positive bias structure emerges and disappears.

S4 and S5 - Software tools to relate observations in STM pictures to experimental parameters.

We developed three Python scripts (Displayer, Tagger and Analyzer), which allow to tag STM images according to the structural features they show. The scripts relate these features to selected experimental parameters stored in the raw images, such as the sample bias voltage and the current setpoint, by creating a color-coded figure. In figure 4, the occurrence of specific structures (different colors) is displayed vs the sample bias and current is displayed. Also, Figures S4 and S5 shows the observed structures vs ratio and dilution, respectively.

**S4: Observed structures as a function of the concentration**
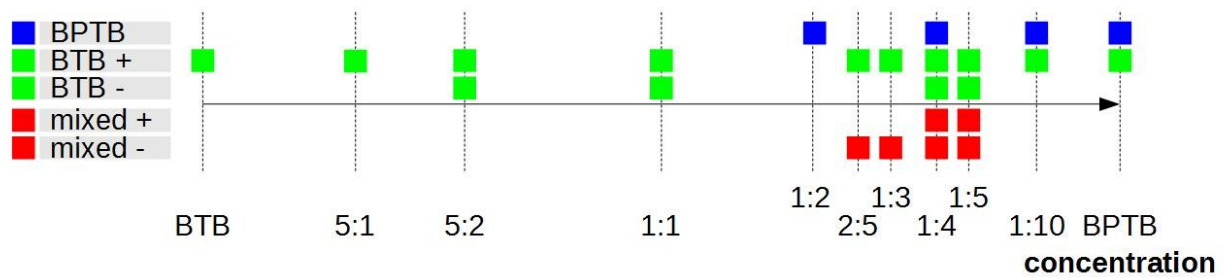
S4: Observed supramolecular structures dependent on the BTB:BPTB mixing ratio. Pure phases are shown above, mixed phases below the arrow. At a given concentration, a structure is marked if at least one sample with this concentration showed that structure. The mixed negative bias structure is observed at BTB:BPTB ratios of 2:5 and lower. The bias-dependent polymorphs and the switching behavior between them is observed at ratios of 1:4 and 1:5.

S5: Observed structures by dilution
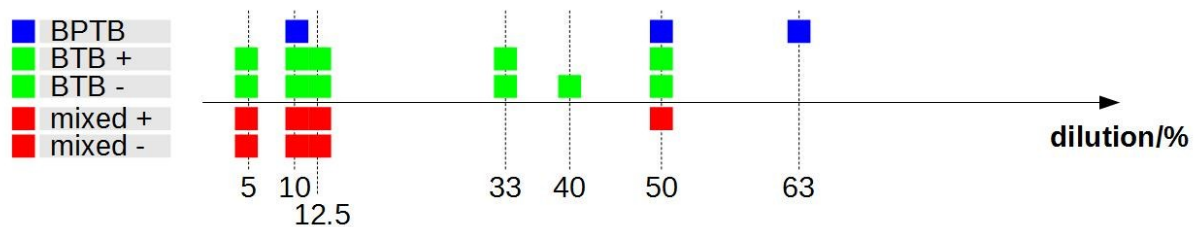
S5: Observed supramolecular structures at different dilutions (volume BTB+BPTP)/(total volume). The 2 µl n-nonanoic acid was added only to compensate for evaporation and was excluded from this calculation. At a given dilution, a structure is marked if at least one sample with this dilution showed the structure. Five samples had individual values between 9 and 12.5% dilution and are shown as larger bars. No link between dilution and a favored polymorph is observed.

S6: Domains of BPTB in mixed negative bias phase, pure BPTP at positive and negative bias
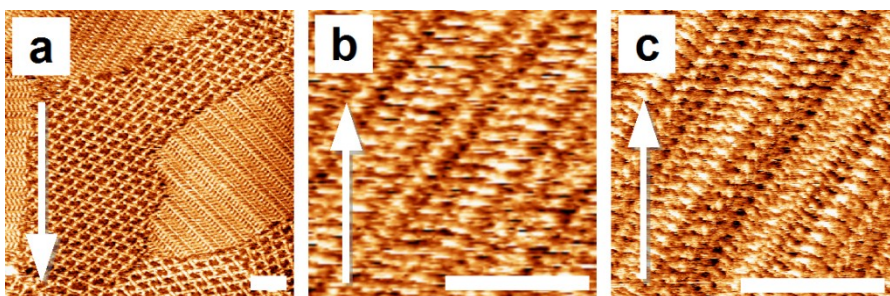
S6: Constant current STM images. Scale bars are 10 nm. Arrows indicate the scanning direction. (a) BTB:BPTB 1:5 50% diluted, U = -850 mV, I = 26 pA, scan rate 3.55 Hz. Domains of pure BPTP form among the mixed negative bias structure. (b) Pure BPTP at positive bias U = 734 mV, I = 122 pA, scan rate 3.55 Hz. (c) Pure BPTP at negative bias U = -980 mV, I = 73 pA, scan rate 3.55 Hz.