Electronic Supplementary Information (ESI)

Nanoscale Tailoring of Supramolecular Crystals via an Oriented External Electric Field

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Content of Supporting Information

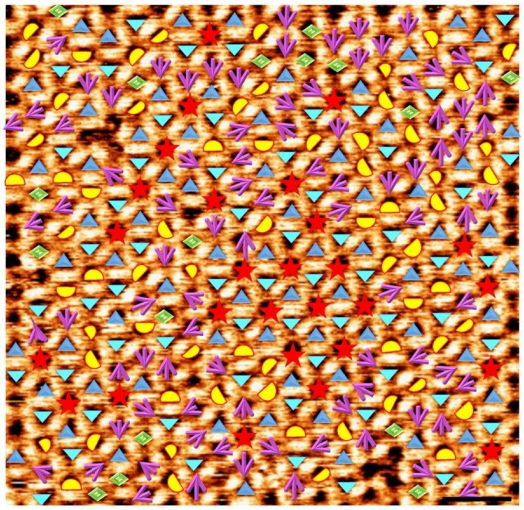

Figure S1. A figure represents the STM image assigning molecular junctions and the glass-like feature in TPTC assemblies. Junctions configuration ratio in a 30x30 nm^2 STM image of TPTC molecular network: The junction configuration is done via labeling each junction point between adjacent molecules by specifying each pore using a symbol to label the di□erent types of junctions. Categorizing the junction type makes it easier to observe the crystallite domain boundaries. The counting was done using the color threshold by choosing all items of a single color and particle analysis functions (to count the number of selected particles) in the STM image.[1]

Table S1 TPTC junction configuration ratios on HOPG to the nearest percentile

Orientations	Total	%
Triangle[A]	136	40.59
Parallelogram[B]	16	4.77
Arrow[C]	89	26.56
Semicircle[D]	67	20.0
Star [E]	27	8.05
Junctions total	335	

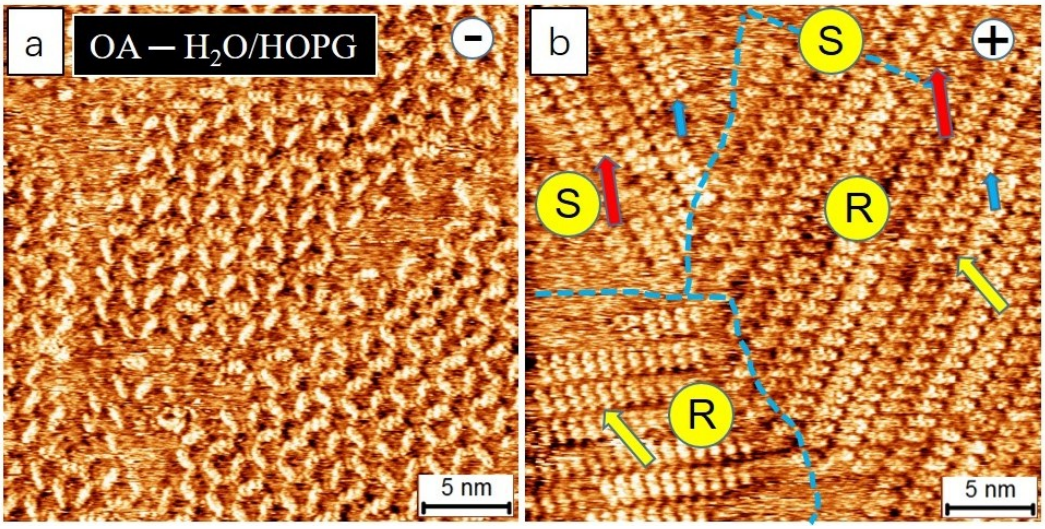

Figure S2. The reversible phase transformations of TPTC electrically triggered by STM at OA-water and HOPG interface. Based on the high-resolution STM image, we found that some head-to-head packing seemly exists within either S or R form domains. As indicated, the blue arrows show the head-to-head orientation in these assemblies while the yellow and red arrows represent the R and S orientations, respectively. However, a head-to-head domain seems not visible after a long time running1 of STM, because eventually all the domains can be defined by either R or S domain via the feature of morei patterns. So, we cannot comment on the typical life span of the metastable state for the head-to-head phase. We have through this representative result offered the R and S form domains and domain boundaries. Imaging conditions (E_{bias}, $i_{tunneling}$) is ±0.9 V, 80 pA.

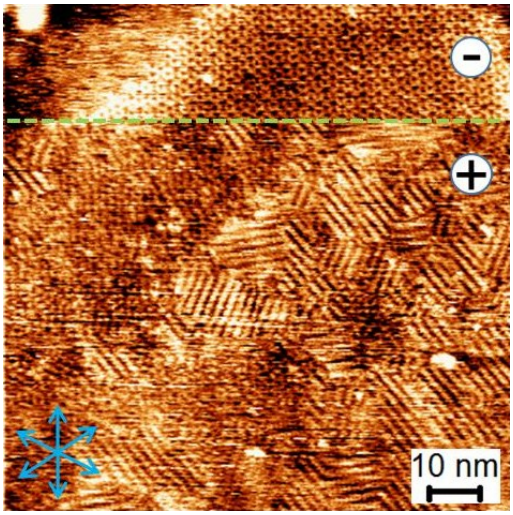

Figure S3. The reversible phase transformations of TPTC electrically triggered by STM at OA and HOPG interface. Imaging conditions (E_{bias}, $i_{tunneling}$) is ±0.9 V, 100 pA.

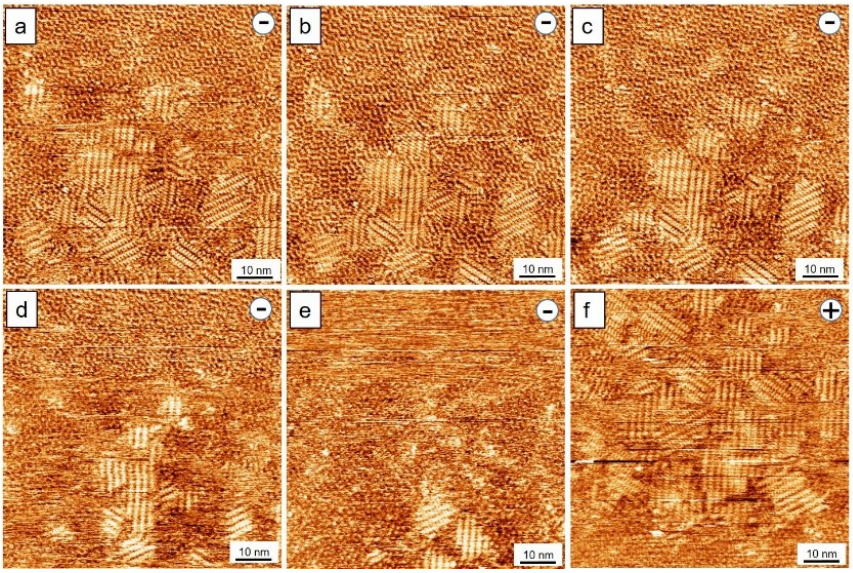

Figure S4. The time-dependent STM images showing the reversible patterning controlled by STM polarity. The images show that the close packing(s) disappear gradually after switching STM polarity from positive to negative. Around 15 mins later, these patterns can be replaced by the random-tilling glass-like assemblies. By doing so, the surface refreshes, referred to as the "clean-out" process. Again, switching the STM polarity from negative to positive can lead to the close packing(s) to appear; the close packing(s) reach 80% coverage over the scanned surface for ca. 30 mins later. (E_{bias}, $i_{tunneling}$) is ±0.9 V, 70 pA.

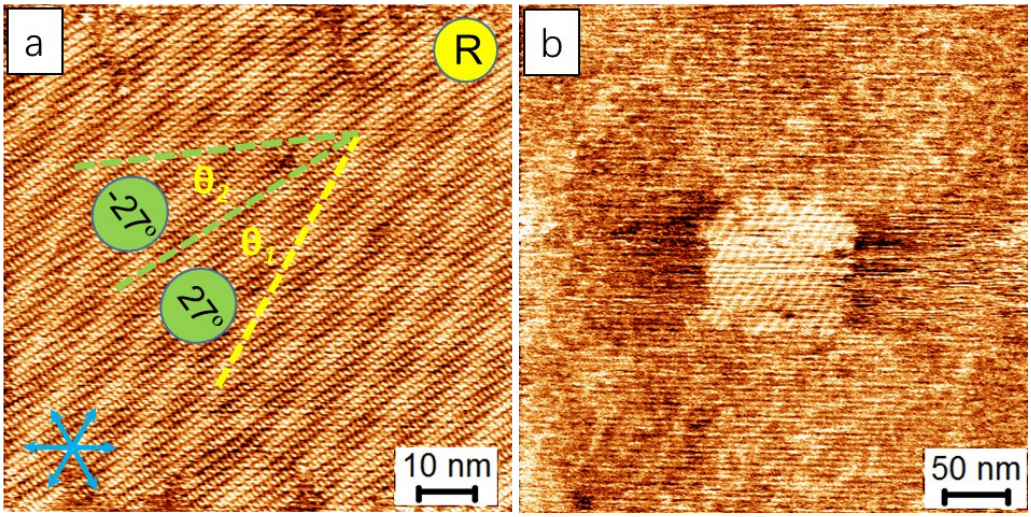

Figure S5. STM images demonstrating the nanoscale local manipulation of crystal growth. Imaging conditions (E_{bias}, $i_{tunneling}$) is 0.17 V, 70 pA.

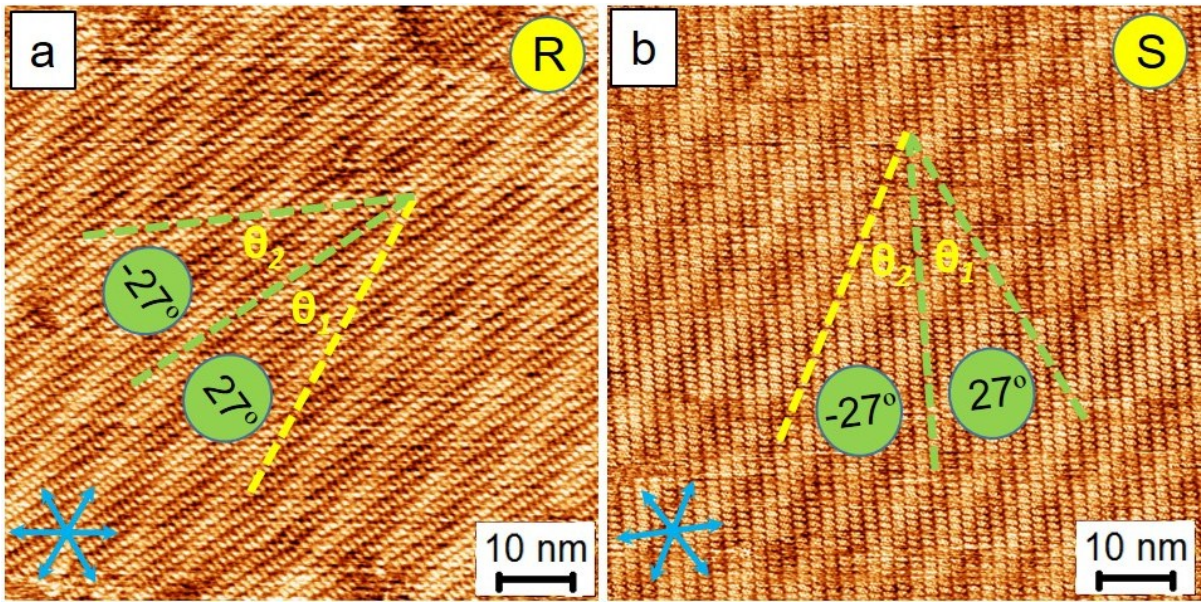

Figure S6. Figure 6 in the main text.

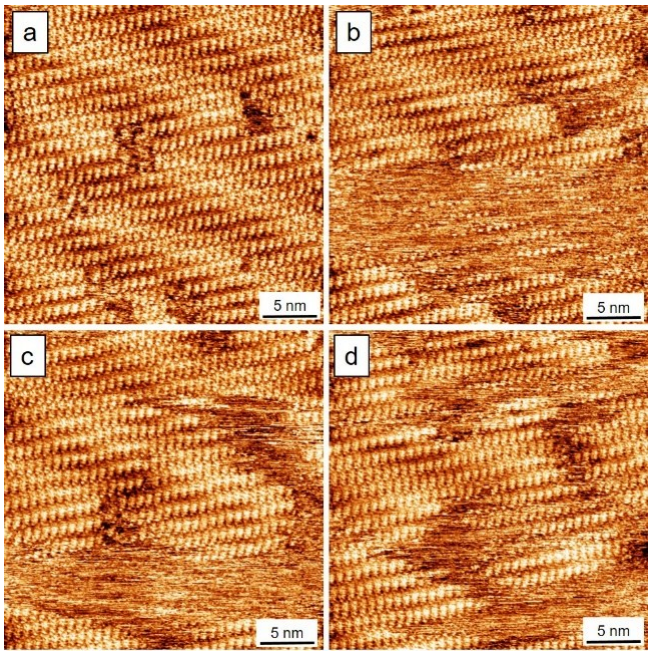

Figure S7. Influence of the current set-point. The results suggest that a higher tunneling current can perturb the close packing likely resulting from closer distance between tip and molecular thin films. (E_{bias}, $i_{tunneling}$) is 0.9 V, 200 pA.

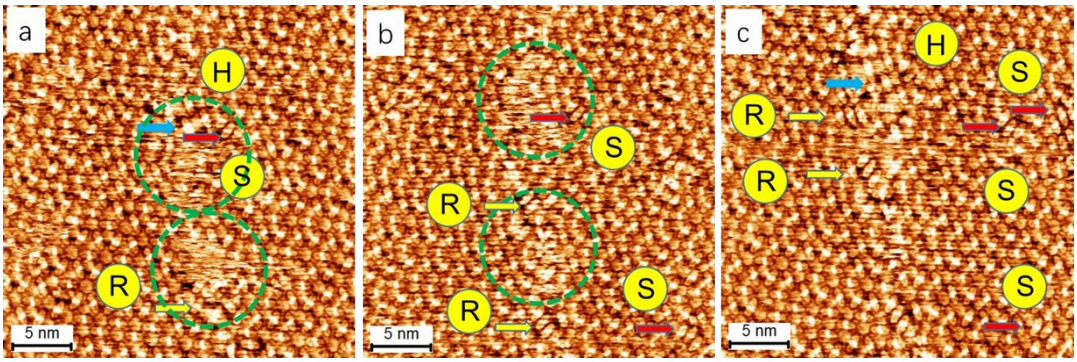

Figure S8. STM images revealing the nucleation and early crystal growths after the appearance of the fuzzy surfaces of fast dynamics. The results show that the nucleation and early crystal growths for R and S forms are relatively much more stable than that of the head-to-head packing, which may explain why after the long-time running of STM, head-to-head packing is absent on the resulting surface. Imaging conditions (E_{bias}, $i_{tunneling}$) is 0.19 V, 100 pA.

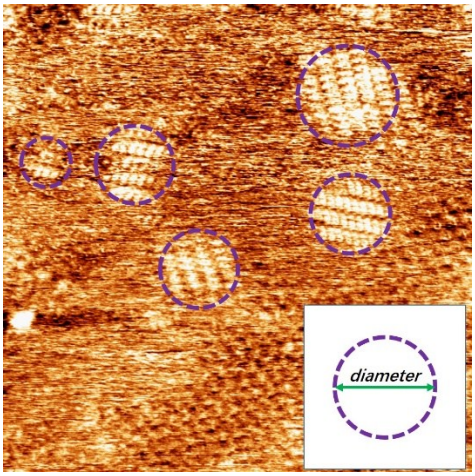

Figure S9. A figure to present how we measure the diameter for a domain size. Briefly, these domains can be roughly considered as either square or rectangle shapes. Circles are drawn to fit in the domains to give the defined diameter(s) in this study. (E_{bias}, $i_{tunneling}$) is 0.9 V, 70 pA.

References

1. M.O. Blunt, J. C. Russell, M. D. C.Gimenez-Lopez Mdel, J. P. Garrahan, X. Lin, M. Schroder, N. R. Champness, P. H. Beton, *Science,* **2008**, 322, 1077.
2. J. P. Garrahan, A. Stannard, M. O. Blunt, M. P. H. Beton, Proc. Natl. Acad. Sci. U.S.A. **2009**, 106, 15209.
3. M. O. Blunt, J. C. Russell, M.D. C Gimenez-Lopez, N. Taleb, X. Lin, M. Schröder, N. R. Champness, P. H. Beton, *Nat. Chem.* **2011**, 3, 74.