Supporting information for:

Ordered Arrays Generated via Metal-Initiated Self-Assembly of Terpyridine Containing Dendrimers and Bridging Ligands

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Origin of images and comparison with HOPG images:

Because of its atomic flatness over large dimensions, relative ease of use and wide-spread availability, HOPG is often used as substrate in scanned probe microscopy studies. However, it has also been shown that freshly-cleaved HOPG, by itself, can give rise to images similar to those ascribed to various adsorbates[1,2].

An additional effect that has been previously reported is the observation of an anomalous superperiodicity on HOPG which gives rise to images reminiscent of those presented here[3-7]. The origin of these images is generally ascribed to Moiré patterns arising from a small-angle rotation (misorientation) between the top and underlying layer(s) of the HOPG substrate. This rotation creates an angle-dependent super-periodicity P given by:

$$P = \frac{2.45\text{Å}}{[2\times \sin(\theta/2)]} \quad (1)$$

where θ is the angle between the hexagonal lattices that is superimposed on the HOPG image. Most recently, it has been reported that this may not be the sole origin for the observed superperiodicity[8,9].

The origin of these supperlattice peaks is schematically depicted in Fig. A where two hexagonal lattices are rotated by 4° and the generation of a hexagonal pattern is readily apparent. However, the detailed properties of these images and their dependence on

experimental variables allow us to unambiguously rule them out as responsible for the images reported here.

1.Whereas the Moiré patterns have the same periodicity along all three directions, for the dendrimers the periodicity is different along one direction as shown in Fig. 3 in the manuscript.

2. Although we have also observed these Moiré patterns (see for example Fig. B), their occurrence is relatively uncommon and are more prone to be seen on lower quality HOPG samples. More importantly, the periodicity of these supperlattices can vary broadly (reported values range from about 2-8 nm) as it depends on the angle of rotation as described in equation 1 above. In the case of the dendrimer films, the variations in size are very small and are only due to the convolution of tip and sample geometries. Moreover, the sizes determined form the images are in excellent agreement with theoretical calculations of the different dendrimers.

3.The contrast of the Moiré patterns is highly dependent on the applied bias, whereas the dendrimer film shows little dependence on the bias.

4.In the Moiré patterns, the undistorted HOPG lattice can still be observed (as grainy features), this not being the case for images of the dendrimer films (see Fig. C).

5.The high reproducibility of the images for the dendrimer films (we have observed the ordered arrays in better than 90% of all samples investigated) would be very unlikely for a Moiré pattern as it would imply having a high density of defects over many, if not all high quality HOPG samples. Moreover, such images were not observed prior to film deposition.

6.In some cases we have observed extremely long isolated 1-D strands (see Fig. D) of the dendrimers and such images would be virtually impossible to arise from Moiré patterns.

We believe that the above provides compelling evidence allowing us to unambiguously rule out the possibility that the images presented arise from Moiré patterns.

References:

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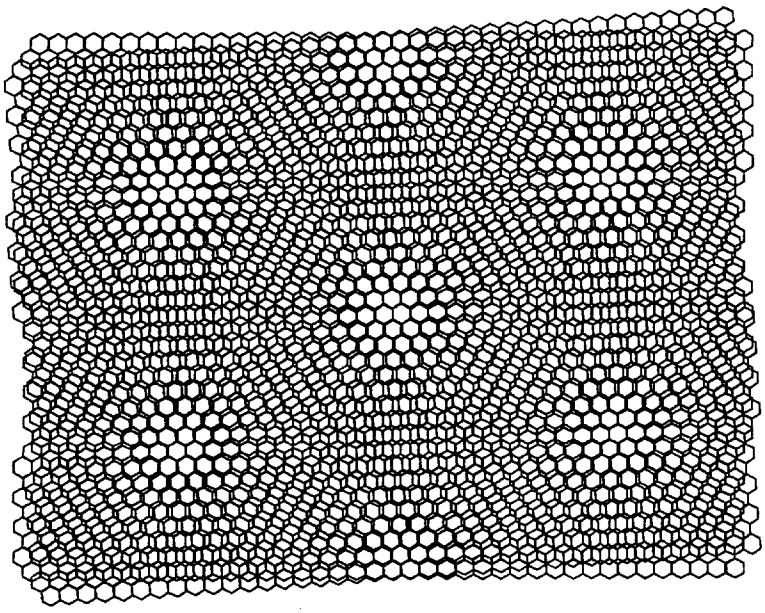

Figure A. Moiré pattern generated by the superposition of two hexagonal layers rotated by 4° relative to each other.

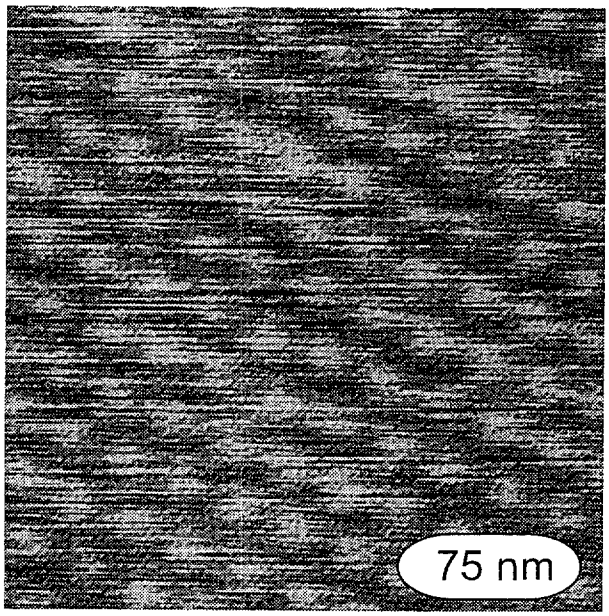

Figure B. Moiré pattern observed on a freshly cleaved HOPG sample.

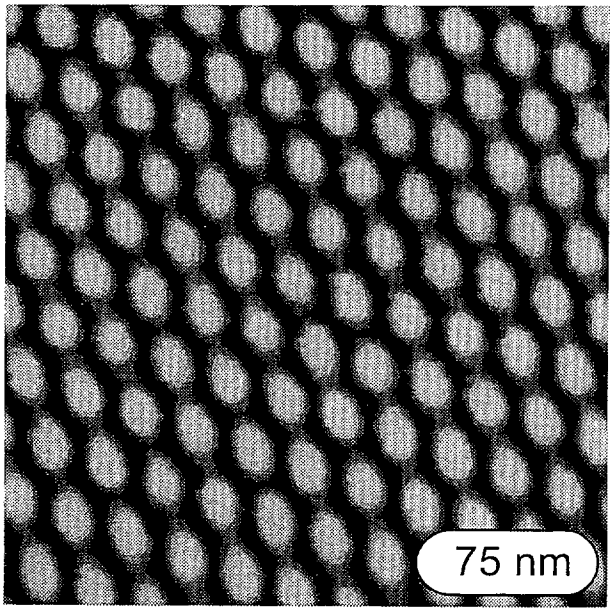

Figure C. STM Image of the dend-8-tpy film on HOPG.

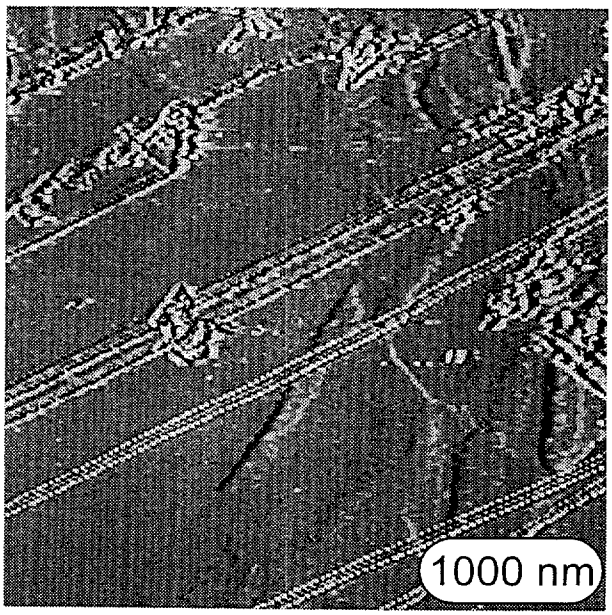

Figure D. Fiber-like strands of dend-8-tpy observed on HOPG; note scale.