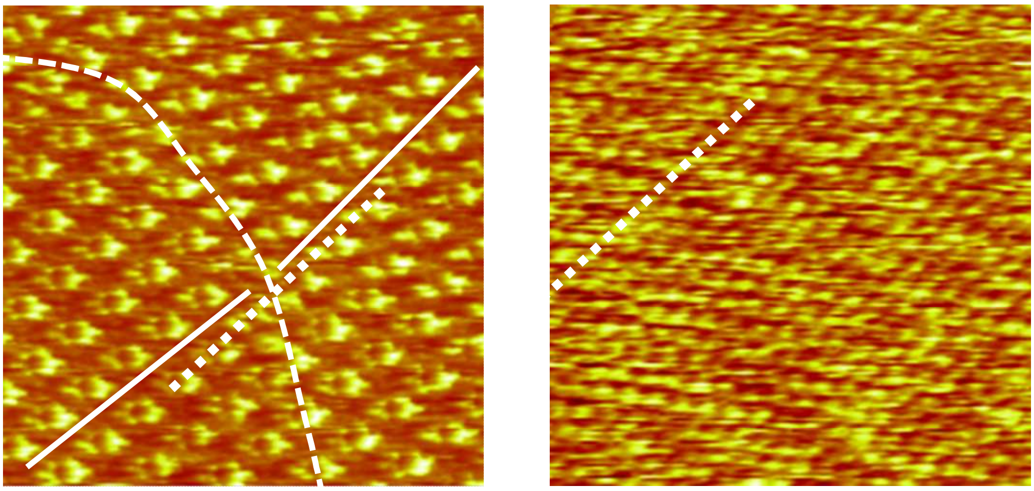
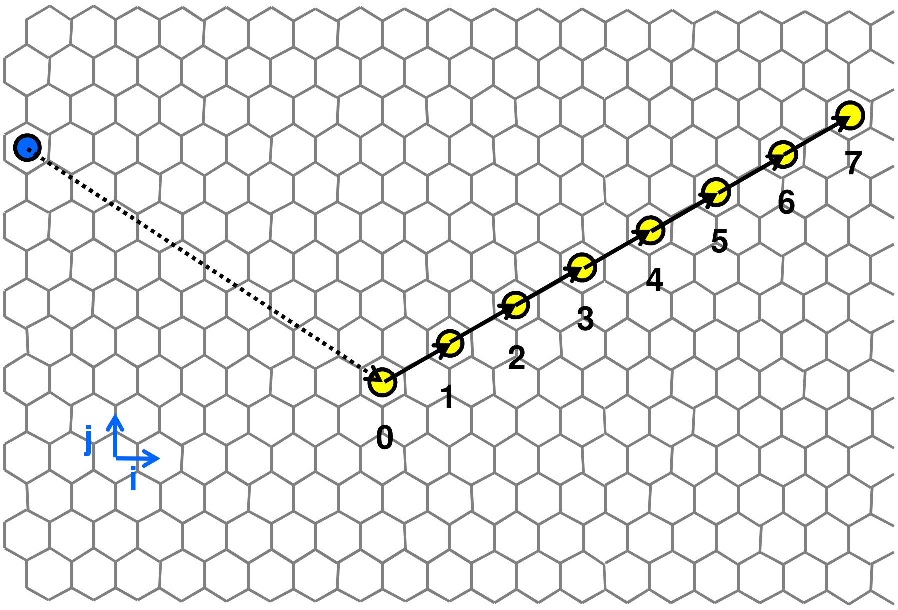
Supplementary material

1. **Direct comparison of molecular lattice orientation and HOPG <110> axis.**



Comparison of a Scanning Tunneling Microscopy images taken on the same area of a self-assembled nanoporous network obtained with TSB3,5-C10. Left: with imaging parameters adapted to molecular imaging (Setpoint: 12pA, sample bias: -0.9V). Right: with imaging parameters adapted to atomic resolution on the HOPG substrate (Setpoint: 900pA, sample bias: -0.28V). Both images were acquired within a 30 second time interval, in the current- (*i.e.* constant-height) mode at fast frame rate (4.8s per frame) in order to reduce the drift. Both images are corrected by home-made software for the drift of the instrument, which was evaluated by correlating successively-acquired images with opposite slow-scan direction. The <100> direction of the substrate is highlighted with a dotted line (right image) and reproduced on the molecular network (left image). The lattice directions of the mirror-symmetric domains (solid lines) form angles of +5° and -2° with the separately measured <100> direction of HOPG, in good agreement with the values expected from the model (±3.2°), within experimental errors inherent to this two-step measurement.

2. Derivation of the lattice epitaxial registry formula



A simplified view of fig. 3.b is represented above. The molecular lattice vectors $\mathbf{p}_n$ are represented (from the origin point in blue to the corresponding point in yellow) for each number n of methylene pairs in the alkyl chain (from the extrapolated value n = 0 up to n = 7 which corresponds to *TSB3*,5-C14). It appears that this vector is the sum of a vector **u** (dotted arrow) and n times a vector **v** (solid arrow). The orthonormal basis we consider in the following is represented in blue in the lower left corner. The unit vectors have the size of HOPG unit vector. Vector **i** is oriented along the <100> direction. In this basis, we have:

$\mathbf{u} = 8\mathbf{i} - 9/\sqrt{3}\mathbf{j}$

$\mathbf{v} = 3/2\mathbf{i} + 3/2\sqrt{3}\mathbf{j}$

then $\mathbf{p}_n = \mathbf{u} + n\mathbf{v} = (\frac{16+3n}{2})\mathbf{i} + (\frac{-18+3n}{2\sqrt{3}})\mathbf{j}$

and $|\mathbf{p}_n| = \sqrt{\left(\frac{16+3n}{2}\right)^2 + \left(\frac{-18+3n}{2\sqrt{3}}\right)^2}$

and finally: $|\mathbf{p}_n| = \sqrt{91 + 15n + 3n^2}$

The angle θ made with the vector i is such that

$\tan\theta = \pm \frac{\left(\frac{-18+3n}{2\sqrt{3}}\right)}{\left(\frac{16+3n}{2}\right)}$

and finally: $\tan\theta = \pm \sqrt{3}\frac{n-6}{3n+16}$