

## Polymorphism and metal-induced structural transformation in 5,5'-bis(4-pyridyl)(2,2'-bispyrimidine) adlayers on Au(111)

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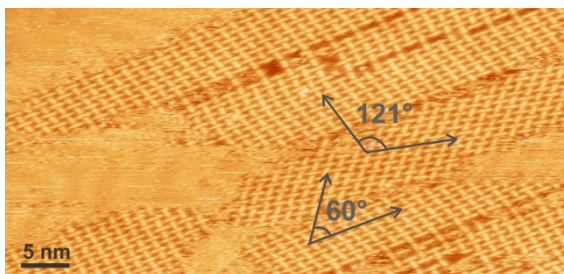
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### Domain rotation

As expected for a substrate templated self-assembly, the domains are rotated by  $120^\circ$  in accord with the symmetry of the Au(111) symmetry. Figure SI1 shows an example for PBP (Phase II) on Au(111) highlighting the rotation between two domains.



**Figure SI.1.** STM images of phase II of PBP on Au(111) showing different domain. Rotations of  $120^\circ$  and  $60^\circ$  are indicated.

## Coverage-dependence of molecular phases

We performed experiments depositing the molecule at 470 K on the Au(111) substrate held at room temperature (RT) but using different deposition times to achieve different coverages. After that we have roughly estimated the relative population of phase II vs. phases I and III by analyzing STM images. Table 1 summarizes the results:

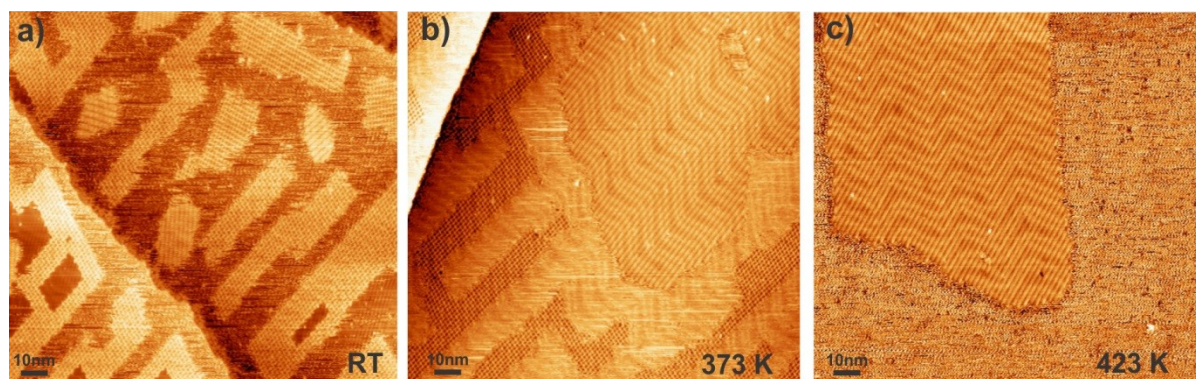
Time (min)	Coverage		
	Phase II	Phase I	Phase III
10	0.1/0.3	-	-
15	0.4		0.1
30	0.4		0.4

**Table I.** Coverage calculated from STM images of PBP molecular phases deposited at the same temperature varying the deposition time from 10, 15 and 30 min.

At lower coverages phase II is the most abundant one, and persists with a 50% abundance at higher coverages. This higher stability for the grid phase compared to linear and zig-zag phases may imply the use of available Au adatoms until their complete use and as soon as the Au adatoms are not available anymore, the other two phases start to appear and compete with phase II.

## Temperature-dependence of molecular phases

We have selected a substrate temperature of 413 K to achieve ordered molecular domains and to promote metal incorporation into the molecular lattices. In addition, we have performed post-annealing of the substrate after molecule deposition. Figure SI.2 shows STM images of PBP on Au(111) at a) RT and followed by post-annealing to b) 373 K and c) 423 K. As is summarized in the images, freshly prepared samples without post-annealing exhibit large population of domains of phase II, whereas increasing the substrate post-annealing temperature up to 373 K increases the relative abundance of phases I and III. Finally at 423 K a similar population of phase II and phases I and III is found. We propose that the Au adatoms that stabilize phase II become more mobile increasing the substrate temperature and are thus capable to reach step edges, where they are trapped, thus resulting in the increased abundance of the adatom-free phases I and III.



**Figure SI.2.** STM images of PBP on Au(111). Post anneal temperature a) RT b) 373 K and c) 423 K.