Supplementary Information for

**Discrete nature of inhomogeneity: The initial stages and local configurations of TiOPc during bilayer growth on Ag(111)**

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A. Substrate Characterization

For the STM experiments Ag(111) films (thickness: 150nm) were used which had been grown epitaxially under high vacuum conditions onto freshly cleaved and carefully degassed mica substrates. The films were prepared in analogy to Au/mica films by using a preparation protocol that is described in detail elsewhere. After transfer of the Ag films into the UHV-system they were cleaned by repeated cycles of Ar⁺ sputtering and annealing. As shown exemplarily in Fig. S1 this treatment yields oxygen-free, clean Ag(111) surfaces which consist of extended, atomically flat terraces revealing a sharp (1x1) LEED pattern.

Figure S1. XPS scans (recorded with hv = 700eV) of a Ag(111)/mica film before and after 3 cleaning cycles, showing, (a), the absence of any remaining carbon and oxygen (red curve), as well as, (b), an excellent long range ordering of the substrate that exhibits atomically flat (111) terraces separated by (mostly) monatomic steps and, (c), the corresponding LEED pattern (E_{kin} = 137eV).
B. Additional SPA-LEED data

**Figure S2.** SPA-LEED images of TiOPc/Ag(111) molecular layers: (a) the POL-phase; (b) the bilayer phase. The corresponding simulated LEED patterns (using the LEEDpat program) are displayed in (c) and (d), respectively. Equivalent domains are indicated by dots of different colors. The white dots (open circles) correspond to reflexes associated with the Ag(111) substrate. Note that the measured images in (a) and (b) have been rotated in order to match the alignment of the simulated pattern (vertical direction corresponds to [11-2] of the Ag(111) surface). The sizes of measured and simulated patterns are adjusted for ease of comparison.

![SPA-LEED images](image)

Superlattice matrix:

\[
\begin{pmatrix}
4.875 & -0.125 \\
2.625 & 5.625
\end{pmatrix}
\]

Surface unit cell size:

\[
A_{\text{POL-phase}} = 199 \text{ Å}^2
\]

\[
A_{\text{Blayer}} = 189 \text{ Å}^2
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**References**
