## **Electronic Supplementary information for:**

## **Self-assembled monolayers of polar molecules on Au(111) surfaces: distributing the dipoles**

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## **Details on the computational methodology**

To simulate the surface we used the repeated slab approach, where 5 layers of gold atoms represented the gold surface and a vacuum gap of > 20 Å was introduced to prevent spurious electronic interactions between consecutive images of the slab in *z*-direction. The dimensions of the real-space unit cell were  $5.11 \times 8.86 \times 45.28$  Å. In that unit cell two molecules are arranged in the typical herringbone pattern (see Figure S1). The *fcc*-hollow was initially chosen as the docking site in the starting geometry. A slight shift of the sulphur atoms towards the bridge site was observed in the optimized geometry. As start values for the tilt angle of the long molecular axis relative to the surface normal, we choose 11.1° and 12.4° for the bipyrimidine 'down' and 'up' conformations, respectively. The mono- and terpyrimidine systems were optimized starting from the converged geometry of the respective bipyrimidine by removing or adding one pyrimidine ring.

We performed DFT calculations (VASP 5.2 code<sup>1</sup>) using a plane wave basis set (cutoff energy: 20.13 Ryd) and a PW91 exchange-correlation functional. The PW91 functional was chosen because it was found to perform slightly better for systems where van der Waals interaction is present<sup>2</sup> (compared to other semilocal functionals). An 8×5×1 Monkhorst-Pack grid of *k*-points was used to sample the reciprocal unit cell. Electronic ( $\Delta E < 0.1 \text{ meV}$ ) and dipole ( $\Delta \mu < 0.003 \text{ eÅ}$ ) convergence were tested carefully. To optimize the geometry, all atoms of the monolayer and the top two gold layers were relaxed until the maximum force component was < 0.01 eV/Å. We employed the external tool GADGET<sup>3</sup> to perform the geometry optimization in internal coordinates.



Figure S1: Top-view of the SAM in the typical herringbone pattern; the unit cell is indicated.

## References (supplementary information)

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- <sup>2</sup> S. Tsuzuki and H. P. Luthi, J. Chem. Phys. 2001, **114**, 3949
- <sup>3</sup> T. Bučko, J. Hafner and J. G. Ángyán, J. Chem. Phys. 2005, **122**, 124508