Supplementary Information

One Dimensional Molecular Dipole Chain Arrays on Graphite via Nanoscale Phase Separation

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1. Large-scale STM images of 0.8 ML ClAlPc on HOPG

Our ClAlPc films were prepared by deposition of ClAlPc on graphite surface at room temperature without further annealing. In this case, before the HOPG surface is fully covered, ClAlPc molecules can aggregate into either single-layer or bi-layer islands with irregular shapes on the graphite terraces.

As shown in Figure S1, the HOPG surface is covered with 0.8 ML ClAlPc. Figure S1(a) (150×150 nm^2) shows the formation of a single-layer ClAlPc island (right) with irregular edge (white dashed line) and the coexistence of HOPG surface with diffused molecules (left, loosely packed ClAlPc layer). Figure S1 (b) (50×50 nm^2) demonstrates a single-layer + bi-layer island, where the HOPG surface with diffused molecules (loosely packed ClAlPc layer) can also be observed at the left side of the image.

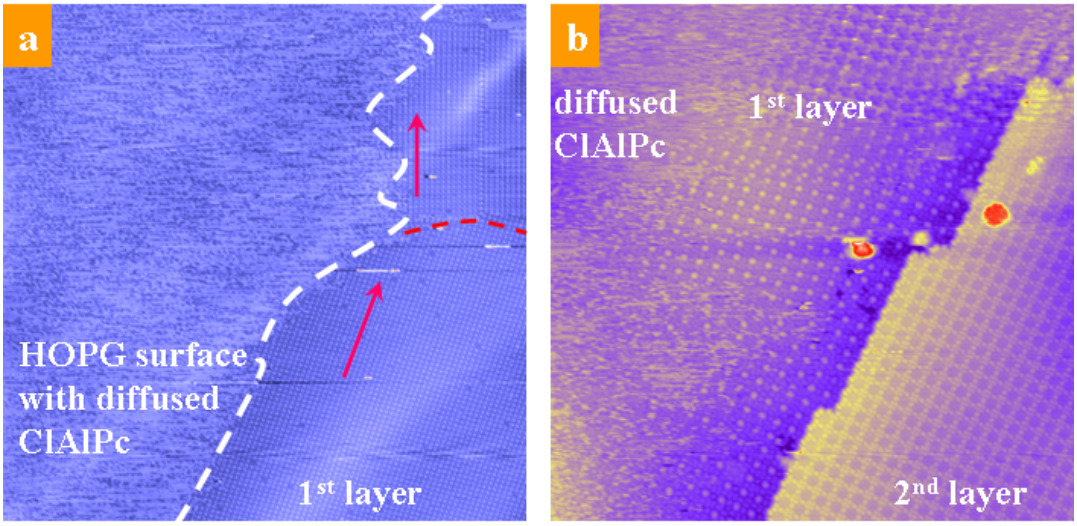

Figure S1 Large-scaled STM images demonstrate the formation of the single-layer + bi-layer ClAlPc film at 0.8 ML coverage. (a) 150×150 nm^2, V_{tip} = 2.4 V; and (b) 50×50 nm^2, V_{tip} = 2.6 V. In panel a, the red arrows denote two different molecular domains with different molecular stripe orientations (top and bottom) in the single-layer island.

2. Detailed analyses of the supramolecular packing structure of the bi-layer ClAlPc film

We suggest that the 1st layer ClAlPc molecules on HOPG adopt Cl-up configuration and the 2nd layer molecules adopt Cl-down configuration based on following justifications:

As shown in figure S2(a), our STM image apparently reveals different molecular features for the 1st layer ClAlPc molecule and the 2nd layer one on HOPG, that is, a four-lobe feature with a bright central protrusion for the 1st layer and with a central depression for the 2nd layer. As revealed in the lateral profile of Figure S2(b), the protrusion is of ~1 Å higher than its sounding lobes and the depression is of ~0.6 Å lower than its lobes under the same scanning conditions. We intuitively assign the 1st layer molecule with a bright central protrusion to the one with the Cl-up configuration and the 2nd layer molecule with a central depression to the one with the Cl-down configuration. The 1st monolayer ClAlPc adopting the Cl-up configuration on the graphite surface can maximize the interfacial π-π interaction between the molecule and substrate. Through close inspections of the edges of the bi-layer islands, we found that the 2nd layer ClAlPc molecules adsorb on the 4-fold hollow site of the 1st layer of ClAlPc (as shown in Figure S2(d)). Such packing structure of the bilayer film can

enhance the electrostatic interaction between dipolar ClAlPc molecules with opposite dipole orientations.

Our assignments of the molecular orientation of the 1st and 2nd layer ClAlPc on HOPG is consistent with previous observations by metastable atom electron spectroscopy and ultra-violet photoemission (UPS) study for ClAlPc on HOPG.[1] Similar stacking configurations have been also widely observed in other dipole and non-planar phthalocyanine thin films, such as OTiPc on HOPG,[2] SnPc on Ag(111),[3] ClAlPc on MoS_2[4] and so on.

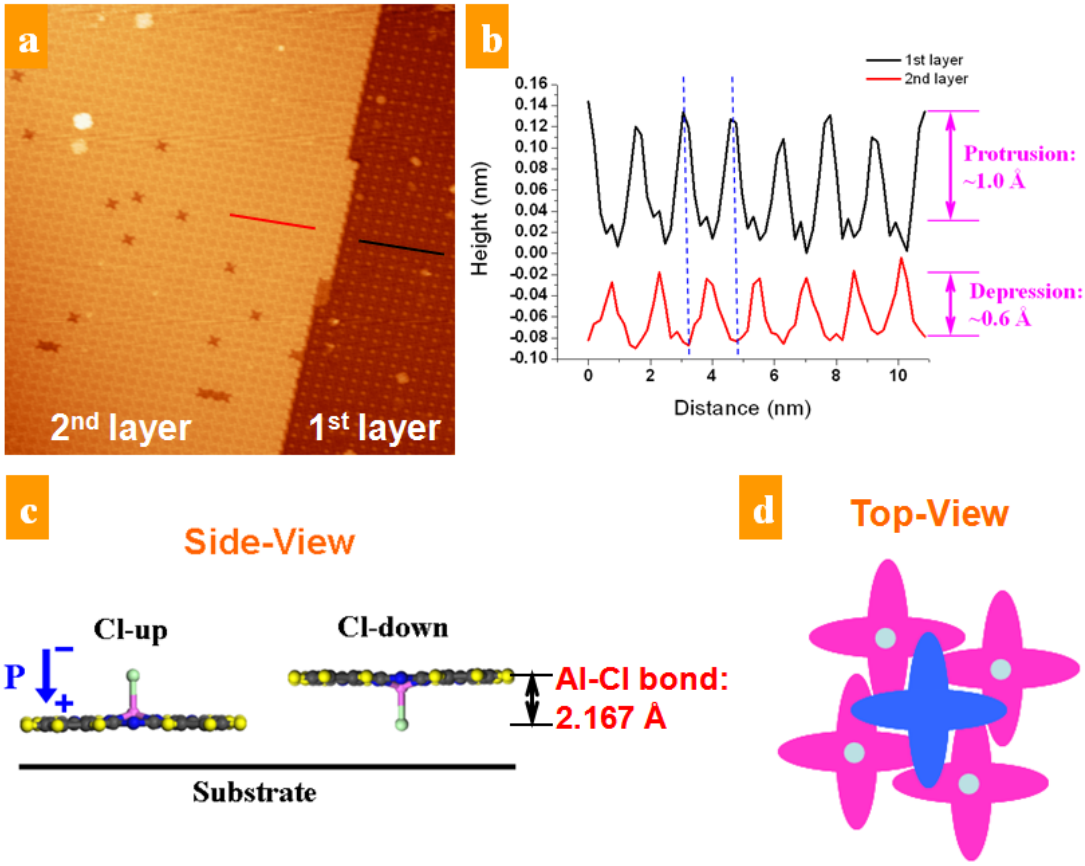

Figure S2 (a) The formation of the single-layer + bi-layer ClAlPc film (60 × 60 nm^2, V_{tip} = 2.8 V). (b) The lateral profiles corresponding to the black and red lines in panel (a), reveal a 1.0 Å protrusion for the 1st layer ClAlPc molecule and a 0.6 Å depression for the 2nd layer one. The blue dashed lines indicate the positions of the molecular centers of the 1st and 2nd layer ClAlPc molecules. (c) Side views of ClAlPc molecules adsorbed on a substrate with Cl-up and Cl-down configurations respectively. (d) Proposed stacking structure of the ClAlPc bi-layer film, where the purple molecules represent the 1st layer molecules with Cl-up configuration and the blue one represents the 2nd layer molecule with Cl-down configuration.

3. Defects in the 1st monolayer of ClAlPc on HOPG

In the 1st monolayer, most of the ClAlPc molecules adopt the Cl-up configuration and appear as four-lobe features with central protrusion. There are two kinds of defects observed in the 1st monolayer as shown in the high-resolution STM image of Figure S3. The molecule with brighter contrast compared to its surrounding molecules at both positive (indicated by purple arrows) and negative tip

bias is suggested to be a ClAlPc molecule with Cl-down configuration in the 1st layer. The molecule with dimmer contrast (denoted by green arrows) is attributed to an impurity from the ClAlPc molecular source. One possible impurity source is H_2Pc without the central ClAl compound.

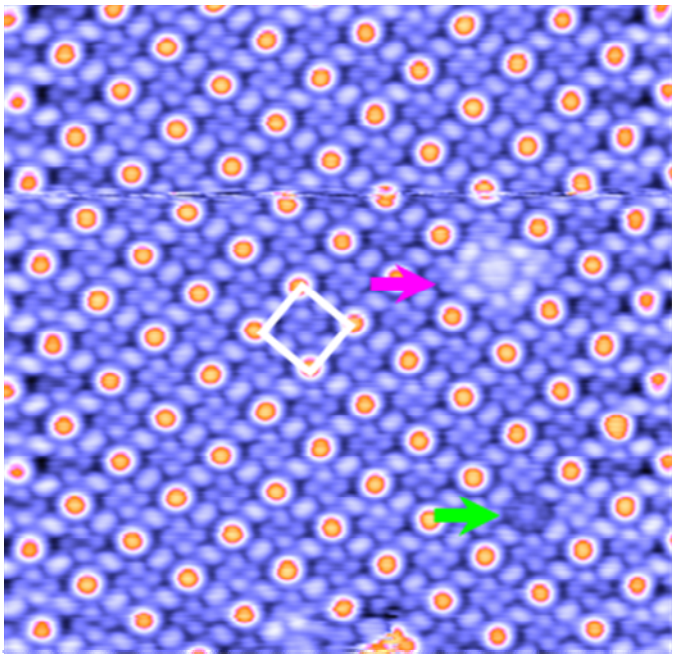

Figure S3 High-resolution STM image shows the single-layer ClAlPc film on HOPG (15×15 nm^2, V_{tip} = 2.4 V), where the purple arrow indicates a Cl-down ClAlPc molecule and the green one refers to an impurity.

References:

1. S. Kera, H. Yamane, H. Honda, H. Fukagawa, K. K. Okudaira and N. Ueno, *Surf. Sci.*, 2004, **566-568**, 571.
2. H. Fukagawa, H. Yamane, S. Kera, K. K. Okudaira and N. Ueno, *Phys. Rev. B*, 2006, **73**, 041302.
3. Y. Wang, J. Krőger, R. Berndt and W. Hofer, *Angew. Chem. Int. Ed.*, 2009, **48**, 1261.
4. Y. Azuma, T. Yokota, S. Kera, M Aoki, K. K. Okudaira, Y. Harada, and N. Ueno, *Thin Solid Films*, 1998, **327–329**, 303.