

Supporting Information

Close-packed arrangements of flat-on free-base porphyrins driven by van der Waals epitaxy

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1. Wetting layer of H₂TPP on DKP:FA

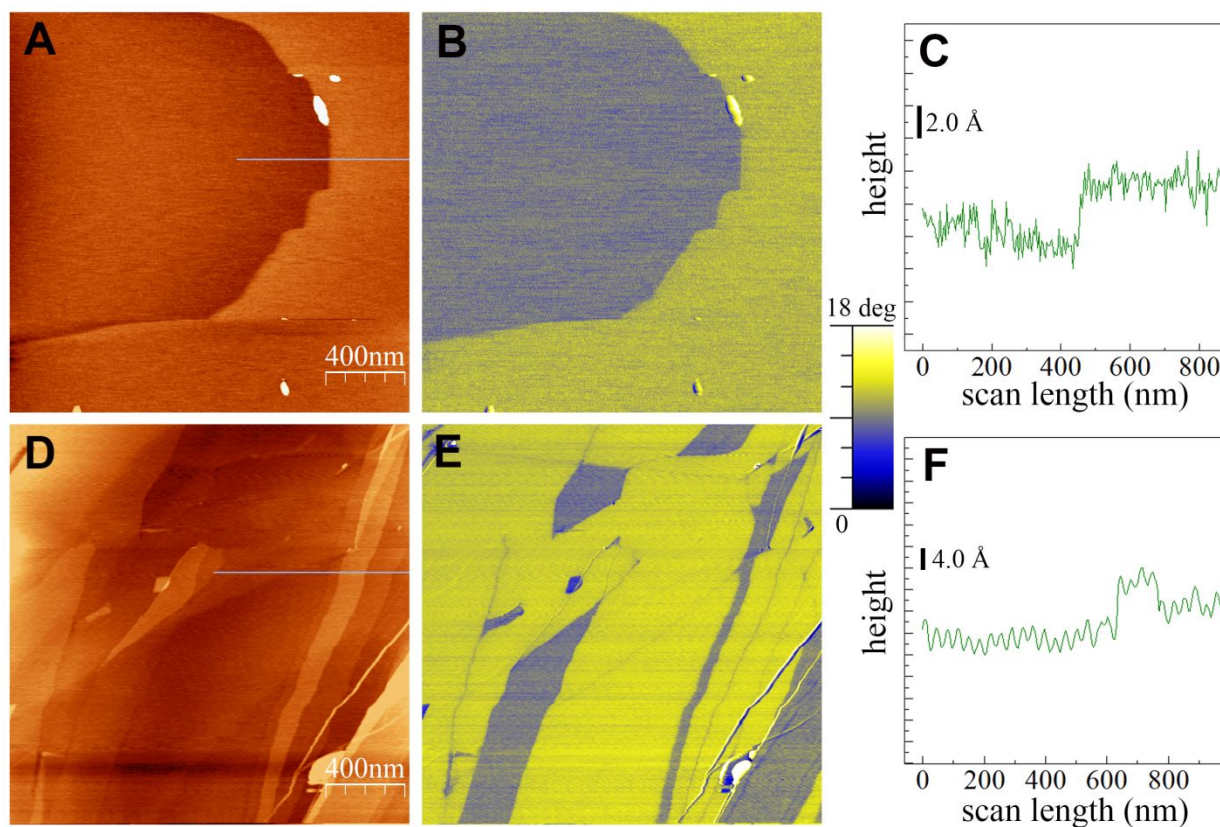


Figure S1. A, D) Intermittent-contact mode AFM topographical images showing 0.5 Å-thick H₂TPP thin films deposited on DKP:FA(110) and HOPG(0001), respectively. C, F) Cross-sectional profiles as taken along the horizontal scan line indicated by the blue segments. B, E) phase-lag signal of the forced cantilever oscillation highlighting the presence of a two-level contrast (see color scale) given by the bare substrate (blue) and organic overlayer (yellow).

2. H₂TPP on DKP:FA adsorption geometry

Key geometrical parameters of the two H₂TPP adsorption geometries on DKP:FA(110) are reported in Figure S1 and Table S1 and compared to the DFT gas-phase geometry.

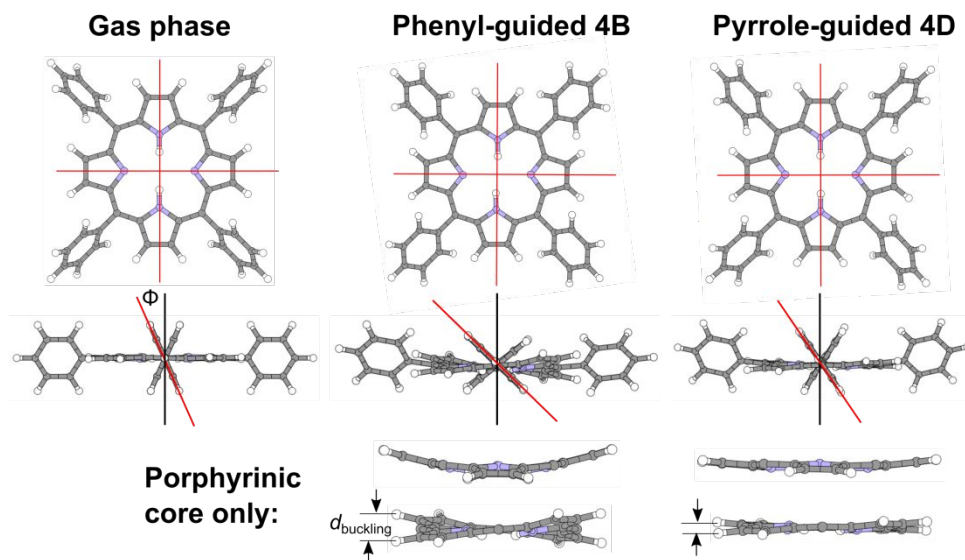


Figure S2. Geometries of the gas-phase and adsorbed H_2TPP molecules (top), and of the inner tetrapyrrole macrocycles (bottom). Ball-and-stick models are shown from various angles. Porphyrinic cores of the adsorbed molecules are saddle shaped.

Table S2. Key geometric parameters of H_2TPP adsorption on DKP:FA(110).

	Gas phase	Phenyl-guided (Figure 4B)	Pyrrole-guided (Figure 4D)
d_{buckling} (Å)	0.00	1.45	0.61
Average phenyl rotation Φ (deg.)	24	47	35
Mean distance to DKP:FA plane (Å)	-	3.58	3.66
Mean porphyrinic core distance to plane (Å)	-	3.41	3.41
Minimum distance to plane (Å)	-	1.97	1.75