

ADVANCED MATERIALS

Supporting Information

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Supplementary Material:

Growth mode induced narrowing of optical spectra of an organic adlayer

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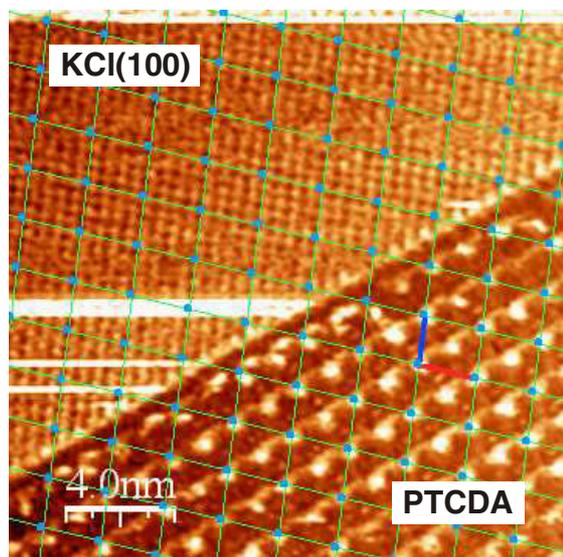
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I. Confirmation of the commensurate epitaxy in the first PTCDA monolayer

An additional AFM image of a PTCDA (sub-)monolayer on KCl(100) is presented. The AFM dissipation signal (Supplementary Figure 1, see *Experimental*) shows the KCl(100) surface lattice (upper part, only every second ion is imaged) as well as the quadratic structure of the first PTCDA monolayer (lower right part). The superimposed grid of lines is simultaneously in registry with each of the two lattices providing visual evidence for the commensurate epitaxy of the PTCDA phase in the first monolayer on top of the KCl(100) surface.



Supplementary Figure 1. Dissipation signal of a PTCDA island at a KCl step edge. The commensurability is deduced between the KCl structure in the upper left part of the image and the quadratic PTCDA phase in the lower right. (Acquisition parameters: $f_0 = 154$ kHz, $A_0 = 3$ nm, $\Delta f = 110$ Hz)

II. Potential energy calculations and phase transition

In addition to the calculation results presented in the paper, we focus on the influence of the number of contributing layers here. The molecular force field calculations were performed as described in the *Experimental* section. The binding energies of PTCDA molecules in layers thicker than one monolayer were calculated, assuming the PTCDA motif to be unchanged from that of the first monolayer (results in Supplementary Table 1). Besides the total binding energy value per molecule, E_{total} , its two constituents E_{intra} and E_{inter} are also given. E_{intra} denotes the interactions between a PTCDA molecule in the specified layer and all other molecules in the same layer, whereas E_{inter} is the sum of the interactions between the said molecule and all molecules in subjacent PTCDA layers as well as with all ions in the two layer KCl substrate. Again, it was crucial to include electrostatic interaction by using partially charged molecules and charged KCl, as outlined in the *Experimental* section.

Supplementary Table 1. Potential energy calculation results as function of layer number for PTCDA on KCl(100). Binding energy values calculated for molecules in different layers of both phases. Values are given per molecule.

Phase	Layer number	E_{inter} (kcal/mol)	E_{intra} (kcal/mol)	E_{total} (kcal/mol)
SQ _{calc}	1.	-37.17	-4.62	-41.79
SQ _{calc}	2.	-32.30	-4.62	-36.92
HB _{calc}	1.	-22.74	-11.74	-34.48
HB _{calc}	2.	-38.70	-11.74	-50.44
HB _{calc}	3.	-40.26	-11.74	-52.00

We already pointed out in the main text that the position of the PTCDA in the unit cell and therefore the structure is mainly governed by strong molecule-substrate interactions. The Coulomb force between the carbonyl oxygens and the potassium ions, which energetically favours the square commensurate phase (SQ_{calc}) of the first PTCDA monolayer, is only feasible due to the appropriate lattice constant of KCl. Consequently, the energetically most favourable HB phase (HB_{calc}) is characterised by a significantly lower binding energy per molecule in the first monolayer, since contributions by Coulomb interactions are reduced. The rectangular unit cell exhibits point-on-line coincident epitaxy with respect to the KCl surface lattice and contains two PTCDA molecules, aligned in a HB motif (cf. structure images in Table 1 of the paper). However, the HB arrangement represents in general an energetically more favourable arrangement of PTCDA molecules in terms of the intralayer binding energy E_{intra} . With the influence of the KCl substrate on the PTCDA molecules diminishing with increasing film thickness, the total binding energy of PTCDA molecules in an assumed second SQ layer is already lower than that in the second layer of a HB domain. This readily explains why we were unable to observe SQ domains thicker than one monolayer and HB domains of monolayer thickness. The fact that the HB phase's E_{inter} magnitude is increasing with film thickness leads to the dewetting of this phase from the KCl surface, i.e., the observed formation of 3D crystallites. However, the HB phase is only energetically more favourable than the SQ phase *after* there are no more free commensurate sites

available on the KCl surface, i.e., a SQ monolayer is completed. In the initial stage of film growth, which is characterised by dominant substrate influence, only domains of the SQ phase form, and external impetus such as thermal annealing or continued evaporation is required to promote/facilitate the transition to the HB phase.