Electronic Supplementary Information

Pentagonal tiling with buckybowls: Pentamethylcorannulene on Cu(111)

Laura Zoppi,^a Tobias Bauert,^b Jay S. Siegel^a, Kim K. Baldridge,^a and K.-H. Ernst*^{a,b}

^a Organic Chemistry Institute, University Zurich, CH-8057 Zürich, Switzerland.

^b Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland. Fax: +41 58 765 4034; Tel: +41 58 765 43 63; E-mail: <u>karl-heinz.ernst@empa.ch</u>



ESI Figure 1 STM image (30 nm × 30 nm) of the striped phase with packing defects.



ESI Figure 2. Modelling the observed structures with hard pentagons. a) (5 2, 1 8) *pm* striped phase of pentagons. The pentagon size has been derived from molecular dimensions and put into the respective ratio to the Cu(111) substrate unit cell parameters (b). c) Rotator phase created in the same manner. One possible "average unit cell" choice has (3 - 2, 35) periodicity. d) Pentagon-model for the (11 3, -3 8) room temperature structure. Contrary to the previous approach (a-c) the Cu(111) unit cell dimensions plus the (11 3, -3 8) periodicity have been used to determine the occupied molecular space ("size of pentagon"). Free rotation of the pentagons without clashing leads to much larger pentagon areas than observed for the low temperature phases.



ESI Figure 3. Initial (5 2, 1 8) model structure before (left) and after (right) DFT-D modelling. The rectangular (5 2, 1 8) unit cell is also indicated. The DFT optimized (5 2, 1 8) structure shows only minute changes in orientation of the molecules with respect to the initial input structure. However, interdigitation of the methyl groups has improved.



ESI Figure 4. LEED patterns (E = 14 eV) revealing the transition at RT from a (6 3, -3 3) structure (left) with increasing coverage to the (11 3, -3 8) structure (right), including a coexistence of both phases, observed as superposition of their diffraction patterns (middle).



ESI Figure 5. Input structure (left) and DFT-D-optimized $(11 \ 3, -3 \ 8)$ model (right). The model (right) shows an irregular distribution of the molecules within the unit cell, which is not observed experimentally.



ESI Figure 6. Initial (10 3, -3 7) model structure (left) and DFT-D-optimized (10 3, -3 7) structure, showing an irregular distribution of the molecules within the unit cell. With respect to the (11 3, -3 8) structure (ESI Fig. 5), the molecules moved closer together, governed by a maximum dispersion of CH₃ and CH groups. This is an indication of attractive interactions when entropic contribution from vibrations is ignored.



ESI Figure 7. Long range STM image (80 nm \times 80 nm, U= -1.235 V, I = 455 pA) of the (5 –5, 5 10) *hole phase.*



ESI Figure 8. Initial (5-5, 510) model structure (left) and DFT-D optimized (5-5, 510) structure. Experimental observation and DFT modelling confirm strong attractive interaction of the molecules at low temperatures.



ESI Figure 9. Initial and final phase from DFT-Dmodelling for the hypothetic (6-5, 611) phase.



ESI Figure 10. Initial (5 2, 1 8) model structure before (left) and after (right) DFT modelling without including dispersional forces. The rectangular (5 2, 1 8) unit cell is also indicated.



ESI Figure 11. Input structure (left) and DFT-optimized $(11 \ 3, -3 \ 8)$ model (right). In contrast to ESI Fig. 5, omitting the dispersion interactions does not lead to attraction between the methyl groups.



ESI Figure 12. Input structure (top, left) and DFT-optimized (5-5, 510) model (top, right). Omitting the dispersion interactions pushes the molecules away from each other. "Switching the vdW forces on", by using the DFT-optimized (5-5, 510) model (top, right) as initial set-up for the DFT-D calculation leads exactly again to the *hole phase* (bottom) as shown in Figures 4, ESI 7 and ESI 8. This shows that the vdW interactions are responsible for attractive lateral interactions and that our calculations do not depend on the initial starting condition.



ESI Figure 13. Input structures (left) and DFT-optimized models (right) for the hypothetic (10 3, -3 7) structure (top) and the (6 -5, 6 11) structure (bottom). Switching off the dispersion forces leave the structures basically unchanged.