Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Selection of conformational states in surface self-assembly for a molecule with eight possible pairs of surface enantiomers

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DFT calculations

DFT calculations were performed using the Grid-based projector augmented wave package (GPAW) [1, 2], with a grid-spacing of 0.18Å. The exchange and correlation energy was calculated using the M06-L meta-GGA functional [3], which has been shown to give a good description of short-range dispersive interactions [4]. All structures were relaxed until the forces were below 0.025 eV/ Å. The isolated molecular fragments were further relaxed to 0.01 eV/ Å to fully optimize the angle between the tail and the molecular backbone.

For the calculation of isolated truncated molecules (see figure S1) and isolated pairs of molecular fragments non-periodic boundary conditions were used, with a minimum distance between the molecule and the cell boundary of 6 Å. Calculations of the periodic structure were performed using periodic boundaries in the x-direction only.

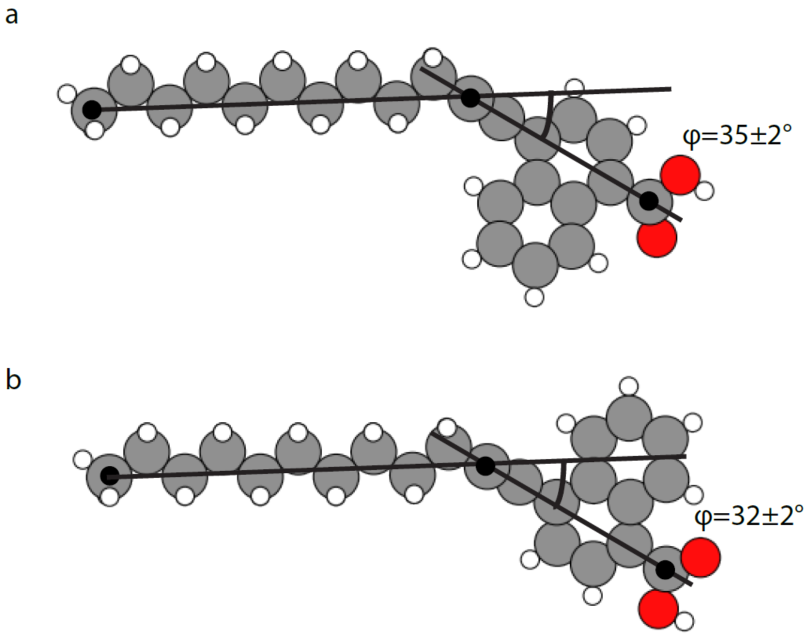

Figure S 1 Energetically favored configuration of a single truncated molecule in the gas phase. The atoms used as fixing points to measure the angle are marked by black dots. The uncertainty on the numbers is estimated by measuring the angle using different atoms as fixing points.

Sequential procedure of the modelling of lamella structure

The DFT based model of the structure, in Fig.1d was determined by a sequential procedure as follows. First the energetically favored orientation of the tail relative to the molecular backbone was determined by making a series of starting configurations with angles in steps of 5° and relaxing each structure with the angle fixed to 0.025 eV/ Å. The lowest energy configurations obtained in this way were further relaxed without constraints to 0.01 eV/ Å. A truncated molecule containing only one naphthalene ring was used to reduce the computational effort (see Fig.S1). The calculations revealed an angle between the molecular backbone and the alkyl tail of 35 (32)° when the naphthalene ring is on the same (opposite) side as the tail, but no energetic preference for the orientation of the naphthalene ring relative to the alkane chain within the computational uncertainties. The calculated angle is in good agreement with the experimentally determined value of (34±2) ° for the molecules sitting in the lamella matrix.

We then considered the relative arrangement of two truncated molecules with the optimum angle between the backbone and the tail, and with the naphthalene ring either on the same side or on opposite side of the backbone relative to the tail (Fig. S2). The two fragments were displaced relative to each other along the direction of the aliphatic chain, as indicated by arrows. The optimum arrangements obtained in this way were then placed in a unit cell with the experimentally determined periodicity along the x-direction. Different orientations of the pairs within the unit cell were used as starting configuration for the relaxation in order to obtain the minimum energy structure for each pair (Fig. 3b and c in the article). Finally, the truncated molecules in the most stable of these structures (Fig. 3b) were replaced by the full molecules (in the most frequently observed LLL conformation) and relaxed to obtain the full structural model shown in Fig 1d.

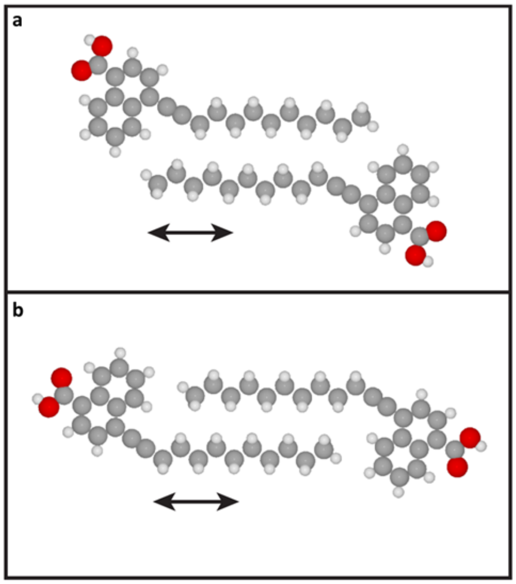

Figure S 2 The most stable truncated molecules coupled pairwise, where the naphthalene unit and the alkyl tail point to the opposite (a) or the same (b) side of the molecular backbone. Each pair is optimized by displacing the fragments relative to each other along the direction of the arrow.

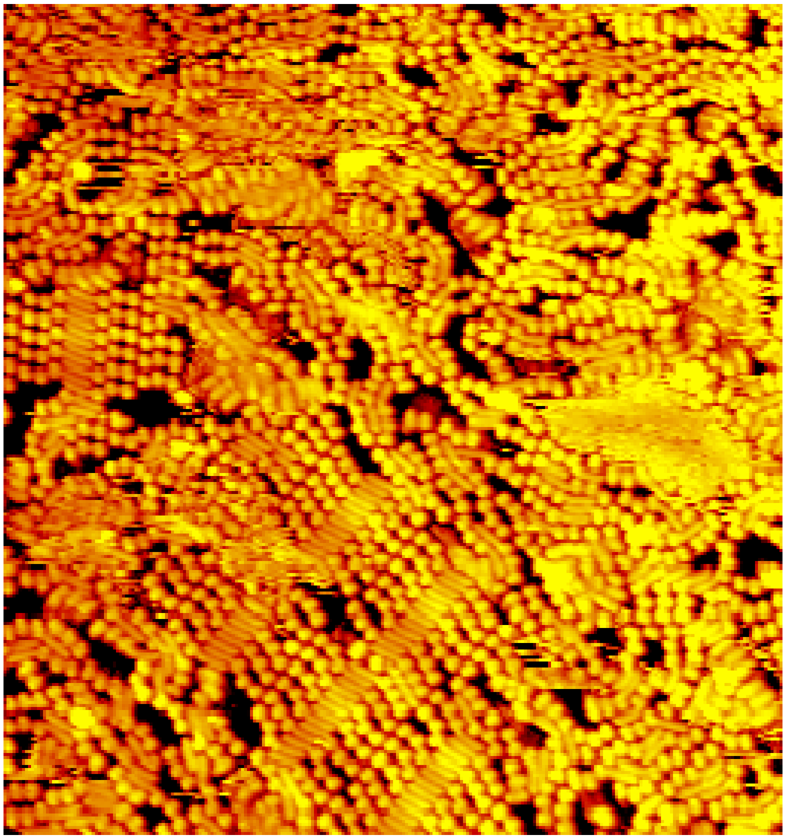

Figure S3 An overview image of the surface with small patches of lamella islands, (390Å×415Å).

Nomenclature of molecular conformations

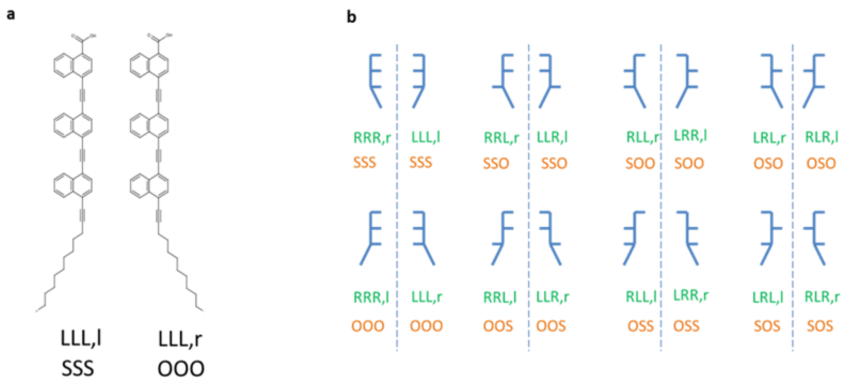

Figure S 4 Scheme explaining the notations of surface conformers: (a) Both the naphthylene units and the decyl chain can be positioned off-axis with respect to the molecular backbone, pointing either to the right or left side. The naphthylene unit orientations are labelled top to bottom order starting from the carboxylic acid group in R/L form. The chain orientation is labelled in r/l. In another set of analysis, orientations of naphthylene units are examined with respect to the chain orientation, from top to bottom, noting whether it is on the same (S) or the opposite (O) side as the alkyl chain (second row, S/O notation). (b) Schematic drawing of all molecular conformations in two different notations.

References

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