

SUPPLEMENTARY INFORMATION

Etching of L-leucine and partial etching of valine crystals

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1. Etching of L-leucine

L-leucine crystals, grown following a similar procedure as for the valine crystals, also expose (001) surfaces when cleaved [see M. Coll *et al.* Acta Cryst. C42, 599 (1986) for the crystallographic structure]. Upon immersion in Milli-Q water such surface shows a similar etch pattern as for L-valine, as shown in Fig. S1. We have not tried with D- and DL-leucine crystals but given the structural similarity with valine we adventure that similar results would be obtained.

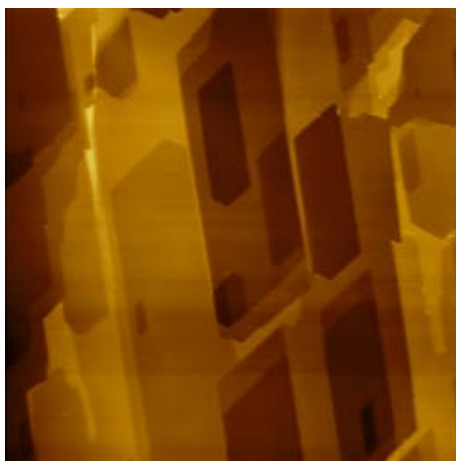


Figure S2. Topography AFM image of a freshly cleaved (001) L-leucine surface after immersion in Milli-Q water taken at ambient conditions. The scale is 10 μm x 10 μm .

2. Partial etching of valine crystals

In order to produce incomplete etching of the surface we have wiped it with a wet cotton (using Milli-Q water) and then dried it immediately with nitrogen. Although the surface becomes also etched by water and well defined patterns appear on the surface, there is a marked difference with the samples prepared by immersion. The most common patterns observed exhibit a trapezoidal shape formed by steps in both the [110] and the [1-10] directions, as shown in Fig. S2.

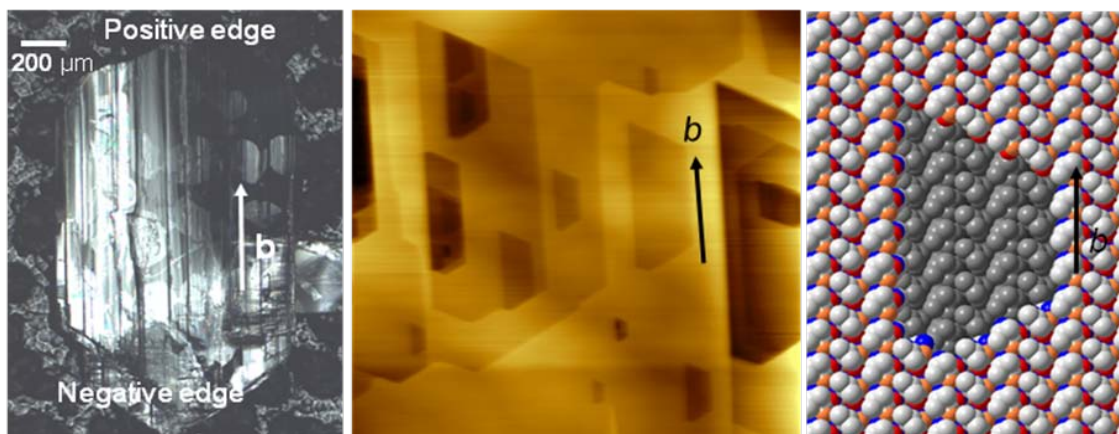


Figure S2. (Left) Optical microscope image of a D-valine crystal. The crystal is polar along b due to the orientation of the valine molecules in the structure. The orientation of the valine dipoles was established by Kelvin Probe Force Microscopy. (Middle) Trapezoidal patterns obtained by wetting the surface using a soaked cotton. (Right) Simulated structure of the trapezoidal patterns. The upper straight step corresponds to a [110] step exposing COO⁻ groups equivalent to the structure obtained by immersion of the crystal. The lower steps correspond to [110] and [1-10] steps exposing NH₃⁺ groups. For immersed crystals only [110] steps were obtained.

Note that the patterns always show one of the edges with only one direction, [110], the direction observed in the immersed samples, and the other edge with both [110] and [1-10] directions. By inspection of the structures of L- and D-valine patterns discussed in the main text it becomes evident that the two steps located at the top and bottom side of the patterns do not have the same structure. The step formed at the lower edge of the pattern is exposing NH₃⁺ groups (positive dipoles) while the step at the higher edge is exposing COO⁻ groups (negative dipoles). In order to identify the chemical nature of the terminations we have used Kelvin Probe Force Microscopy (KPFM), which has been widely used to study surface charges and dipoles [see i.e., A. Verdaguer, M. Cardellach, J. Fraxedas *J. Chem. Phys.* **129**(17), 174705 (2008)]. In order to determine the orientation of the surface dipoles on each edge of the crystal we took a thick valine crystal flake, cut it in two pieces and glue them standing up on a metal substrate, each of them exposing one of the two different edges along the b direction.

We approached a conductive AFM tip [Pt/Ir coated silicon tips with constant $k_c \sim 0.2 \text{ N m}^{-1}$ (PPP-CONTPt, NanoAndMore GmbH, Darmstadt, Germany)] to each edge and perform KPFM measurements. The experiment consisted in applying an *ac* bias, $V = A \sin(\omega t)$, to the tip with a few volts amplitude. The tip interacts with the dipoles on the surface and starts to oscillate at the same frequency ω of the applied bias and at two times this frequency, 2ω . The oscillation at ω can be nulled by applying a *dc* voltage to the tip as in the Kelvin Probe method. The voltage needed to null the amplitude is the contact potential difference between the crystal and the tip. We observed that one edge needs a positive voltage to null ω while the other needs a negative voltage. This means that positive dipoles or charges are present at the positive edge and negative charges or dipoles at the negative edge and thus we were able to identify the positive edge as the edge that exposes NH_3^+ groups and the negative as the edge that exposes COO^- groups. Using this analysis the structure of the steps showed in Fig. S2 was determined. The side of the patterns that only shows [110] steps correspond to steps exposing COO^- groups and the side showing [110] and [1-10] steps correspond to steps exposing NH_3^+ groups.