Electronic Supplementary Material (ESI) for Chemical Communications

Towards a molecule-by-molecule understanding of crystal formation on heteronulcei: Molecular-scale studies of Carbamazepine on Gold

Erin V. Iski, **Error! Reference source not found.**, **Error! Reference source not found.**, E. Charles H. Sykes and Andrew J. Urquhart*

Supplementary Information

Experimental Details

The sample preparation and STM imaging were conducted in a LT UHV Omicron Nanotechnology system with a base pressure < 5 x 10^{-11} mbar. The Au(111) single crystal (MaTeck) was cleaned prior to CBZ deposition by cycles of Ar^+ sputtering (1.0 keV/18 μA) followed by thermal anneals to 1,000 K. The cleanliness of the metal surface was verified by STM imaging. The CBZ sample vial was heated to ~413 K, and the molecules were dosed onto the cold surface *via* sublimation into the STM chamber through a heated gas line and precision leak valve. The molecules were deposited on the samples through a collimated molecular doser. Due to the difficulty in achieving a multi-layer on the surface using the conventional dosing procedure, the cold sample (~78 K) was held in place directly in front of the molecular doser for 2 mins at 1 x 10^{-7} mbar. After dosing, the substrate was annealed to various temperatures so as to modulate coverage and provide thermal energy for molecular ordering to occur. The 160 K anneal was achieved by placing the sample in the room temperature carousel for 5 minutes, while the 220 K anneal was for 10 minutes. Topographic STM imaging was operated under the constant-current mode with the bias applied to the sample. The substrates were kept at 78 K during all STM imaging. All images were recorded with cut Pt/Ir wire tips (80/20, 0.25 mm diameter).

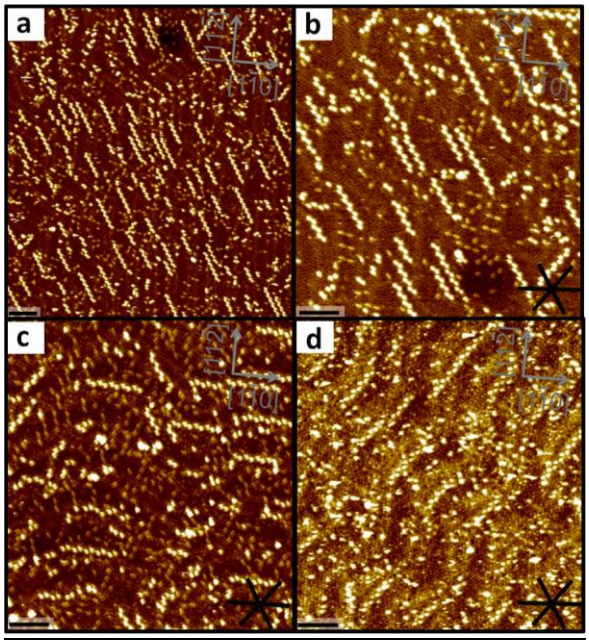

Fig. S1 STM images of CBZ catemeric chains. a) Large-scale STM image showing the formation of ordered chains within the second layer of CBZ on Au(111). I = 35 pA, V = -500 mV, scale bar = 10 nm. b) Smaller-scale STM image indicating the alignment of the chains with the close-packed directions of the substrate (three black lines in each small scale image). I = 25 pA, V = -500 mV, scale bar = 7 nm. c and d) Additional small-scale images indicating how the chains orient in three different directions according to the three-fold symmetry of the underlying atomic lattice. c: I = 35 pA, V = -700 mV, scale bar = 7 nm. d: I = 50 pA, V = -800 mV, scale bar = 7 nm. Gold substrate crystallographic directions shown in grey.

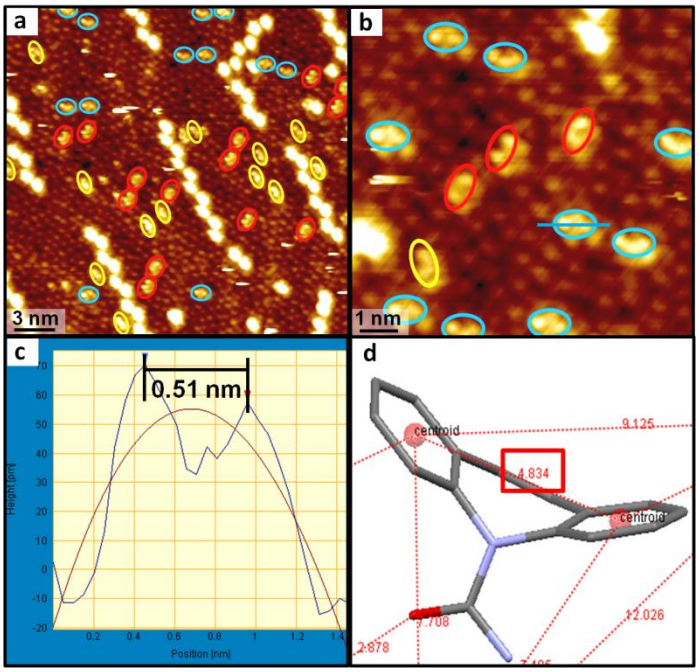

Fig. S2 Orientations of individual second layer molecules not included in the catemer chains. a) The three preferred orientations of the molecules are indicated with coloured ovals. I = 25 pA, V = -500 mV, scale bar = 3 nm. b) A zoomed-in STM image showing the intramolecular resolution of the isolated second layer molecules. I = 25 pA, V = -500 mV, scale bar = 1 nm. c) A line scan of the blue line over the molecule in b indicates that the distance between the two lobes in the second layer CBZ molecule is ~0.5 nm. d) The distance from the line scan is very close to that of the distance between the two aromatic rings of a single CBZ molecule as shown with a stick model of the molecule, which shows a theorized distance of 0.48 nm between the aromatic rings (boxed in red).

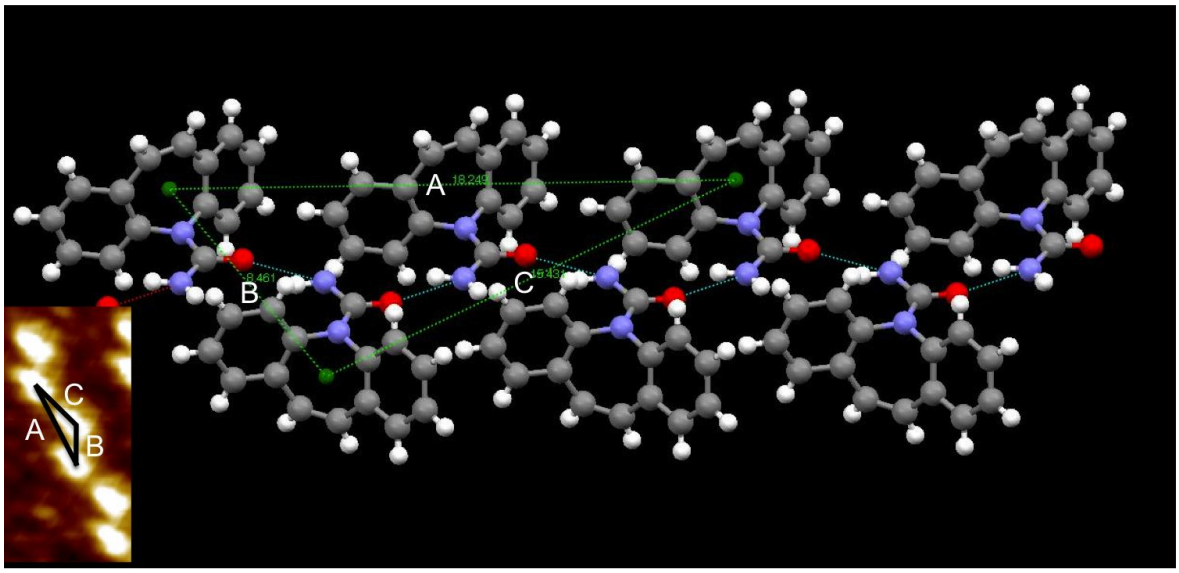

Fig. S3 Crystallographic data of CBZ form V. Form V has three key dimensions (A (18.25 Å), B (8.46 Å) and C (15.43 Å) which closely correlate with the three dimensions in the inset STM image (A (18.5 Å), B (8.50 Å) and C (13.0 Å). For further information on CBZ form V please see Arlin *et al.*, *Chemical Communications*, 2011, **47**, 7074-7076.