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Electronic Supplementary Information (ESI)

Isomerism control of diethylstilbestrol by metal surface induced O-H cleavage

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Contents

Detailed methods

Sample preparation. Samples were prepared in two separate ultra high vacuum (UHV) chambers following the same procedures. The single crystal surfaces of Ag(111) and Cu(111) were prepared by cycles of Ar^+ (Linde, 99.999%) sputtering and annealing to $\sim$ 590–723 K and $\sim$ 733–770 K, respectively. Diethylstilbestrol (DES, Sigma, $\geq$ 99%) was dosed with organic molecular beam epitaxy on the Ag or Cu surfaces by heating of the solid powder to $\sim$ 370–390 K.

STM. An Aarhus-type variable-temperature STM (SPECS GmbH) housed in the analysis chamber of a home-made UHV system at 3×10^{-10} mbar base pressure in Garching was employed. The tip consisted of a chemically etched tungsten wire. Measurements were performed in the constant current mode and the tunnelling bias, U, was applied to the sample. The topography images were processed by the WSxM software.[1]

XPS. The measurements were carried out at the HE-SGM dipole beamline at the BESSY II storage ring in Berlin. The base pressure of the end station was $\sim 1\times10^{-9}$ mbar. The excitation energy for the C 1s and O 1s spectral regions was 435 and 680 eV, respectively. Data were collected in normal emission geometry at a sample temperature of $\sim$ 200 K. The binding energy scale of the spectra was calibrated by setting the Ag $3d_{5/2}$ or Cu $3p_{3/2}$ core levels at 368.3 eV or 75.1 eV, respectively. A Shirley background was subtracted from the raw data.

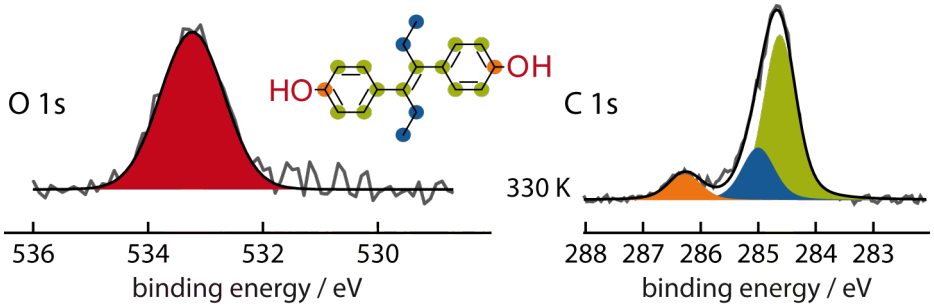

Fig. S1: O 1s and C 1s core levels of a submonolayer coverage of DES on Ag(111) after annealing to 330 K. The inset of the DES structural formula highlights the chemical inequivalent C atoms expected to be distinguished in the C 1s spectra. The same colour code applies to the respective fitted components.

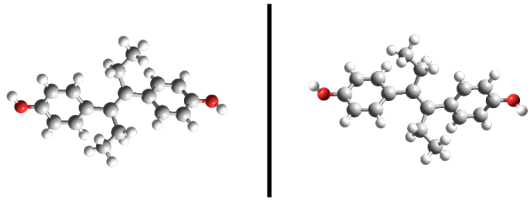

Fig. S2: Surface enantiomers of *trans* DES.

[1]Horcas, I.; Fernández, R.; Gómez-Rodríguez, J. M.; Colchero, J.; Gómez-Herrero, J.; Baro, A. M. *Rev. Sci. Instrum.* **2007,** *78*, 013705.

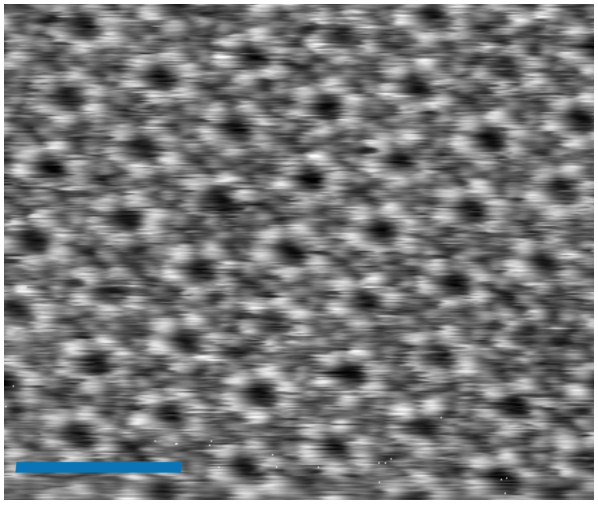

Fig. S3: STM image of the *shingle motif* structure at $\sim$ 150 K showing increased contrast of the less mobile ethyl groups (scale bar = 3 nm, U = 1.25 V, I = 0.13 nA).

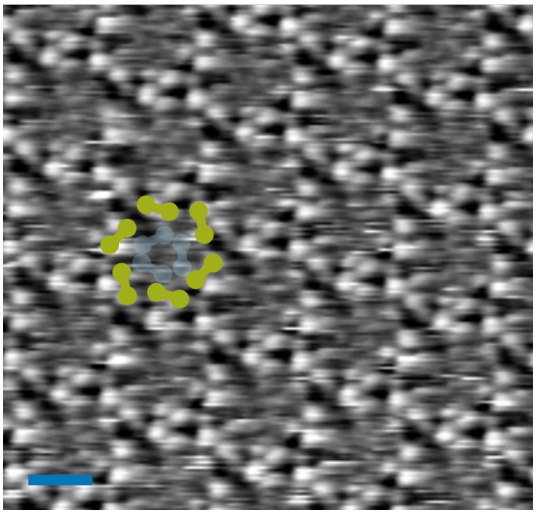

Fig. S4: STM image showing mobile central supramolecular trimers within the *windmill motifs* (scale bar = 2 nm, T = 290 K, U = 1.49 V, I = 0.13 nA).

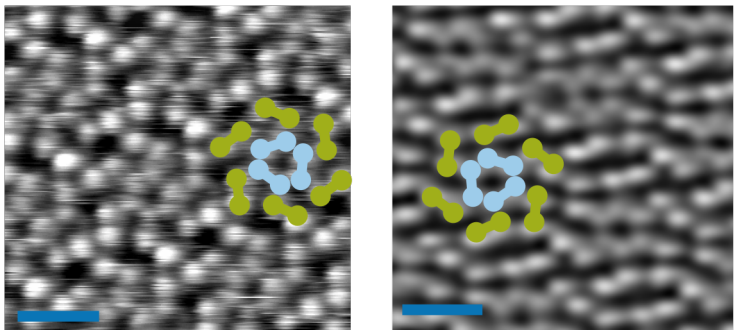

Fig. S5: STM images showing the organisational chirality in *windmill motif* domains. Left: S-domains (scale bar = 2 nm, T = 290 K, U = 1.25 V, I = 0.14 nA). Right: R-domains (scale bar = 2 nm, T = 290 K, U = 1.49 V, I = 0.14 nA).

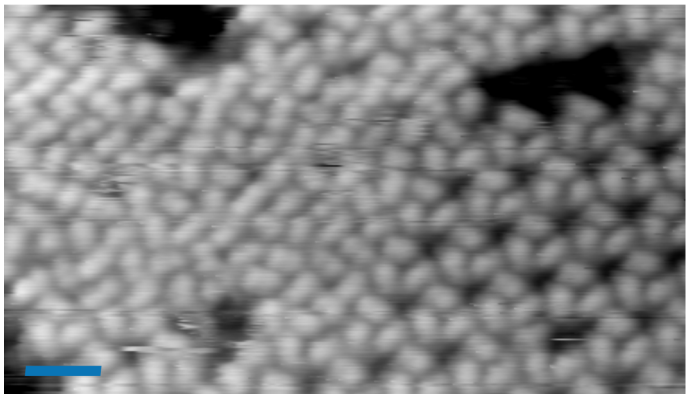

Fig. S6: STM image of DES on Cu(111) (scale bar = 2 nm, T $\sim$ 173 K, U = 2.67 V, I = 0.16 nA). The *star motif* (on the right) fades into a disordered arrangement of these elongated protrusions. If the substructure accounted for more than one molecule, one would also reasonably expect to identify smaller, separate protrusions of single molecules in a disordered phase.

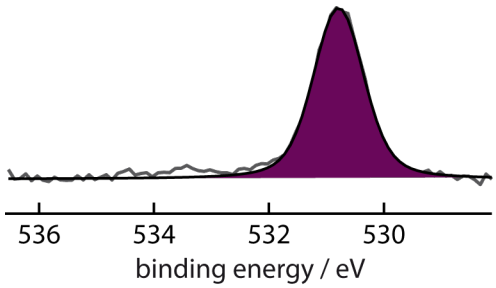

Fig. S7: O 1s signal of a submonolayer coverage of DES on Cu(111) after annealing to 400 K.