## Self-assembly at room temperature of thermally stable discrete and extended oligomers of polycyclic aromatics on Ag(100): induced dipoles and cooperative effects

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## Experimental procedures.

Experiments were carried out in an Omicron VT-STM operated at a base pressure of  $2 \times 10^{-10}$  mbar. STM images were recorded in constant current mode using etched tungsten tips. Voltage values refer to the gap voltage, i.e. to the voltage applied to the tip. The Ag(100) single crystal was cleaned by cycles or Ar<sup>+</sup> sputtering and annealing and the surface condition checked by low energy electron diffraction, Auger electron spectroscopy and STM prior to adsorbate deposition at room temperature. 2-vinylnaphthalene (Aldrich, optical grade, 98%, m.p. ~340 K) was purified by pumping to the sample vial to  $10^{-5}$  mbar and dosed via a leak valve with the vial heated to ~330 K. 1-vinylnaphthalene (Aldrich, optical grade, 95%), being liquid at room temperature, was purified by freeze-pump-thaw cycles and dosed via a leak valve. 2-vinylanthracene (Toronto Research Chemical Inc., 95%) was dosed by sublimation in vacuum at 333 K.



**Figure S1.** STM image of 1-vinylnaphthalene on Ag(100) deposited and acquired at 120 K;  $230 \times 230 \text{ Å}^2$ ,  $V_{\text{gap}} = 0.46 \text{ V}$ ,  $I_t = 0.54 \text{ nA}$ . Some impurities are discerned as depressions in this image. These bear no particular spatial correlation to the ring adsorbate structures. Different surface preparations with the same exposure to 1-vinylnaphthalene and impurities concentration varying by  $\pm 50\%$  yielded similar density of rings.



**Figure S2.** Three consecutive STM images of 1-vinylnaphthalene on Ag(100) acquired at room temperature;  $60 \times 60 \text{ Å}^2$ ,  $V_{gap} = 0.58 \text{ V}$ ,  $I_t = 0.94 \text{ nA}$ .



**Figure S3.** Schematic diagram illustrating a tetramer of 1VN and two fused rings of 1VN resulting from a chirality defect.



**Figure S4.** Schematic diagram illustrating two possible modes of chirality switch/fused ring propagating events for 2-vinylnaphthalene.