Templating molecular adsorption using a covalent organic framework

Supplementary Information:

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Sample preparation:

The samples for all experiments consisted of commercially obtained epitaxial Au(111) films grown on mica substrates. The samples were heated by passing a current through a piece of Si(111) wafer placed behind the sample. The samples were loaded into the UHV system (base pressure < 1×10^{-10}Torr) and thoroughly degassed up to temperatures > 600°C. The samples were then cleaned by repeated cycles of Argon sputtering (~5×10^{-6}Torr, ~1.0keV, ~2.0mA for 20 minutes) followed by annealing up to 550°C and controlled cooling. Following each sputtering/annealing cycle the samples were imaged with STM to check cleanliness and the quality of the reconstructed gold surface. The temperature is estimated using fixed temperature points (T~550°C, determined using a pyrometer and room temperature) and the assumption of proportionality between power output of the Si resistive heater and temperature.

Additional STM data:

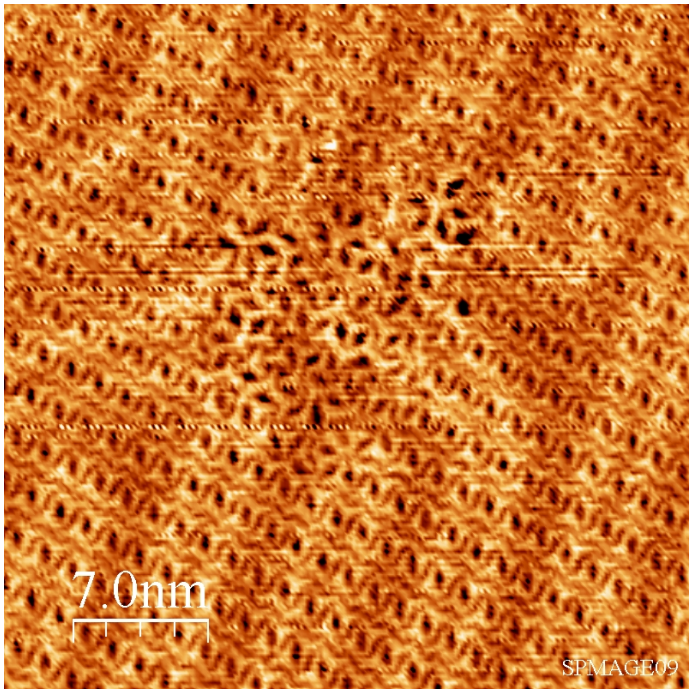

Fig S1: STM image of a complete TBPB monolayer which has been annealed at 110°C for 10mins (same sample as shown in Fig. 1C). The initiation of both dimer and larger more disordered network structure formation at one of the Au(111) herringbone kink sites is clearly apparent.

Density functional calculations of TBPB dimer:

Density functional theory (DFT) calculations of the TBPB dimer were carried out using the DMol[3] package in Materials Studio 4.4. The generalised gradient approximation functional of Perdew-Burke-Enzerhof was implemented[1]. Core electrons were represented by effective core potentials constructed according to the method of Bergner *et. al.*[2] and double numerical basis sets with polarization functions were used for the valence electrons. The radius within which the atomic orbitals are strictly localized was set to 3.7 Å. For geometry optimisations the structure was considered to have converged when the force on the atoms was < 0.1eV $Å^{-1}$. A default convergence tolerance of 10^{-5} eV was employed for the self-consistent field cycle at each stage of the optimization process. Simulations were carried out in the gas phase with no constraints placed on any of the atoms in the molecular structure.

References:

1. J.P. Perdew, K.. Burke and M. Enzerhof, *Phys. Rev*. *Lett.* **1996**, *77*, 3865.
2. A. Bergner, M. Dolg, W. Kuchle, H. Stoll and H. Preuss, *Mol. Phys.*, **1993**, 80, 1431-1441.